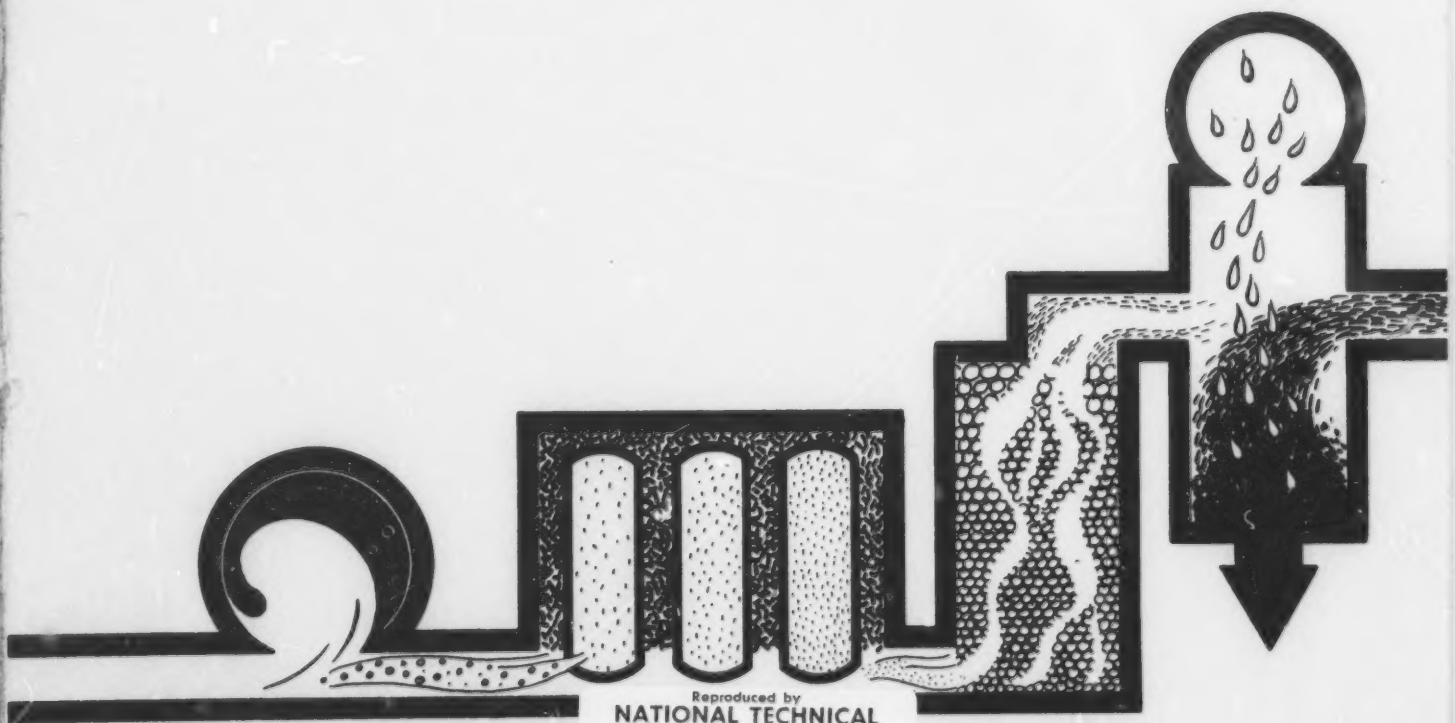
WATER POLLUTION CONTROL RESEARCH SERIES • 17010 EKI 09/71

W72-09388

PB 209 939

Phosphate Precipitation With Ferrous Iron



Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151

U.S. ENVIRONMENTAL PROTECTION AGENCY

71

WATER POLLUTION CONTROL RESEARCH SERIES

The Water Pollution Control Research Series describes the results and progress in the control and abatement of pollution in our Nation's waters. They provide a central source of information on the research, development and demonstration activities in the Environmental Protection Agency, through inhouse research and grants and contracts with Federal, State, and local agencies, research institutions, and industrial organizations.

Inquiries pertaining to Water Pollution Control Research Reports should be directed to the Chief, Publications Branch (Water), Research Information Division, R&M, Environmental Protection Agency, Washington, D.C. 20460.

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

1. Report No.

W72-09388

4. Title: PHOSPHATE PRECIPITATION WITH FERROUS IRON

5. Report Date

6.

8. Performing Organization Report No.

7. Author(s): Ghassemi, M[redacted]; Recht, H[redacted] L.

10. Project No. EPA Project √17010 EKI 09/71

9. Organization: North American Rockwell Corporation, Canoga Park, California, Atomics International Division

11. Contract/Grant No. ~~14-12-917~~

13. Type of Report and Period Covered

12. Sponsoring Organization: Environmental Protection Agency

15. Supplementary Notes: Water Pollution Control Research Series ~~No. 17010 EKI~~, September 1971, 64 p, 6 fig, 17 tab, 18 ref.

16. Abstract: Pure solutions of orthophosphate at concentrations representative of those in wastewater, orthophosphate solutions containing bicarbonate alkalinity, pyro and tri-polyphosphate solutions, and secondary effluent samples from an activated sludge plant were used in batch precipitation tests of phosphate removal by ferrous iron additions. The effects of pH, reactant concentration, and diverse ions on the rate and efficiency of reactant removal were evaluated. For orthophosphate precipitation with Fe(II), a reaction time of 5 hrs., an initial orthophosphate concentration of 12 mg/l, and an Fe(II) to orthophosphate equivalence ratio of 1.0, a maximum orthophosphate removal of 97% was attained at pH 8.0. Reaction time for maximum orthophosphate removal increased with decreasing pH. Reaction speed was independent of Fe(II) concentration but decreased at lower orthophosphate levels. System behavior was the same in secondary effluent as in pure solution. Dissolved oxygen addition increased orthophosphate removal efficiency, but the resulting precipitate was very fine and hard to settle. Comparisons of Fe(II) data with that of Fe(III)-and Al(III)-phosphate systems are included. (Lowry-Texas)

17a. Descriptors: *Phosphate, *Chemical precipitation, *Separation techniques, Iron compounds, Hydrogen ion concentration, Dissolved oxygen, Oxidation, Aeration, Sedimentation, Laboratory tests, *Waste water treatment

17b. Identifiers: *Waste pickle liquor

Copy available from GPO Sup Doc [redacted] . $0.70 ; microfiche from WRIS as PB 209 934 $0.95.

17c. COWRR Field & Group: 05D

18. Availability: ✓

19. Security Class. (Report)

20. Security Class. (Page)

21. No. of Pages

22. Price

Send To:
WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

Abstractor: Mark V. Lowry

Institution: Texas Univ, Austin

PHOSPHATE PRECIPITATION WITH FERROUS IRON

by

Masood Ghassemi
Howard L. Recht
Atomics International
A Division of North American Rockwell Corporation
Canoga Park, California 91304

for the

Office of Research and Monitoring

ENVIRONMENTAL PROTECTION AGENCY

Project #17010 EKI
Contract #14-12-817

September 1971

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402 - Price 70

EPA Review Notice

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

Phosphate removal by ferrous iron addition was studied in batch precipitation tests conducted on pure solutions of ortho-, pyro- and tripolyphosphate, orthophosphate solutions containing bicarbonate ion, and secondary effluent. The effects of pH and reactant concentration on the efficiency of reactant removal were evaluated.

In the absence of dissolved oxygen and for initial conditions of 12 mg/ℓ P and a reactant equivalence ratio of 1.0, orthophosphate removal was maximum (97%) at a pH of 8.0. The precipitate formed was identified as vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$. At this pH and at lower pH levels, Fe(II) removal nearly paralleled that of orthophosphate removal. The time for maximum orthophosphate removal increased with decreasing pH. The reaction speed was independent of Fe(II) concentration but decreased at lower orthophosphate levels. The system behavior was the same in secondary effluent as in pure solutions. Pyro- and tripolyphosphates were less efficiently precipitated than orthophosphate.

Dissolved oxygen increased orthophosphate removal efficiency. However, the precipitates obtained in the treatment of oxygen-containing secondary effluent were usually very fine and did not settle well.

The data on Fe(II)-phosphate precipitation are compared with those of Fe(III)- and Al(III)-phosphate systems.

This report was submitted in fulfillment of Project No. 17010 EKI, Contract 14-12-817, under sponsorship of the Environmental Protection Agency.

CONTENTS

Section		Page
I	Conclusions	1
II	Recommendations	5
III	Introduction	7
IV	Experimental	9
V	Results and Discussion	21
VI	Acknowledgments	61
VII	References	63

FIGURES

No.		Page
1	Schematic Diagram of the Controlled Atmosphere Reaction System	12
2	Controlled Atmosphere Reaction System	13
3	System for Settling Rate Studies	14
4	Sample Removal from Reaction Vessel	17
5	Precipitation of Orthophosphate with Fe(II), Al(III) and Fe(III) at a Cation-to-Orthophosphate Equivalence Ratio of 1.0	29
6	Solubility Diagram for Ferrous Phosphate	45

TABLES

No.		Page
1	Partial Analyses of the Secondary Effluent Samples Used in Various Precipitation Experiments	10
2	Summary of Experiments Discussed in Text	22
3	Changes in Solution Turbidity and pH in Orthophosphate Precipitation with Fe(II)	23
4	Changes in Solution Turbidity and pH in Crthophosphate Precipitation with Fe(II)	24
5	Effect of pH on Orthophosphate Precipitation with Fe(II)	26
6	Orthophosphate Precipitation with Fe(II) at an Fe(II)-to-Orthophosphate Equivalence Ratio of 1.5	32
7	Effect of Orthophosphate Concentration on Phosphate Precipitation with Fe(II)	34
8	Effect of Bicarbonate Alkalinity on the Precipitation of Orthophosphate with Fe(II)	35
9	Orthophosphate Precipitation from Secondary Effluent with Fe(II) in the Absence of Dissolved Oxygen	37
10	Precipitation of Pyro- and Tripolyphosphate with Fe(II) in the Absence of Dissolved Oxygen	39
11	Equilibrium Relationships for Orthophosphate-Fe(II) System	42
12	Orthophosphate Precipitation with Fe(II) in the Presence of Dissolved Oxygen	47
13	Orthophosphate Precipitation with Fe(II) from Secondary Effluent in the Presence of Dissolved Oxygen	49

TABLES (Continued)

No.		Page
14	Formation and Settling Characteristics of Precipitates in Orthophosphate Precipitation from Secondary Effluent with Fe(II) in the Presence of Dissolved Oxygen	52
15	Orthophosphate Precipitation from Secondary Effluent with Fe(II) in the Presence of Dissolved Oxygen - Analysis of the Filtrates	54
16	Settling Characteristics of the Precipitates in Orthophosphate Precipitation from Secondary Effluent with Al(III)	56
17	Settling Characteristics of the Precipitates in Orthophosphate Precipitation from Secondary Effluent with Fe(III)	57

SECTION I

CONCLUSIONS

Atomics International has conducted a parametric investigation of phosphate precipitation using ferrous iron in which the effects of pH, reactant concentration and diverse ions on the rate and efficiency of reactant removal were evaluated. Pure solutions of orthophosphate at concentrations representative of those in wastewater, orthophosphate solutions containing bicarbonate alkalinity, pyro- and tripolyphosphate solutions and secondary effluent samples from an activated sludge treatment plant were used in this investigation. To establish background data on the aqueous chemistry of phosphate-Fe(II) reactions, the majority of the experiments were conducted in the absence of dissolved oxygen (to prevent oxidation of ferrous iron to ferric iron) in a special controlled atmosphere reaction system, which also allowed for continuous monitoring of solution pH and periodic removal of sample aliquots for analysis of turbidity and determination of residual reactant concentrations. Only a limited number of tests were performed on phosphate solutions containing dissolved oxygen. The precipitates obtained in various experiments were observed for color characteristics and some were also examined by x-ray diffraction for chemical structure. Using a special sampling apparatus, the settling properties of the precipitates formed in the treatment of secondary effluent with Fe(II) in the presence of dissolved oxygen were evaluated and the results were compared with similar data obtained using Al(III) and Fe(III) salts.

The data collected on orthophosphate precipitation with Fe(II) in the absence of dissolved oxygen indicated the following:

(a) The efficiency of orthophosphate removal with Fe(II) is strongly pH dependent with the maximum removal obtained in the vicinity of pH 8. For a reaction time of 5 hr, an initial orthophosphate concentration of 12 mg/ℓ P, and an Fe(II)-to-orthophosphate equivalence ratio of 1, the maximum levels of reactant removal were 7, 35, 94, 69, and 18% for orthophosphate and 9, 39, 97, ~ 100, and ~ 100% for ferrous iron in experiments conducted at initial pH levels of 6, 7, 8, 9, and 10, respectively.

(b) The rate of reactant removal is generally more rapid at higher pH levels. For an orthophosphate concentration of 12 mg/ℓ P and a reactant equivalence ratio of 1, there was no increase in the extent

of reactant removal after 5 min at pH's of 9 and 10, whereas at pH 8 a reaction time of about 2 hr was required to achieve maximum reactant removal.

(c) The speed of reactant removal appears to be unaffected by changes in the Fe(II) concentration but is affected by changes in pH and orthophosphate concentration. For an orthophosphate concentration of 12 mg/ℓ P and an initial pH of 8, the patterns of change in pH, turbidity, residual reactant concentration, and precipitate color were nearly the same for Fe(II)-to-orthophosphate equivalence ratios of 1.5, 1.0, and 0.33. For an Fe(II) concentration of 3.87×10^{-4} eq/ℓ and at the optimum phosphate removal pH, the reaction was more rapid at an orthophosphate level of 12 mg/ℓ P than at 4 mg/ℓ P.

(d) At the optimum precipitation pH and at lower pH levels, not all of the excess ferrous iron added to the phosphate solution precipitates with the phosphate or as hydroxide.

(e) In the vicinity of the optimum precipitation pH, bicarbonate alkalinity at a concentration of 420 mg/ℓ $NaHCO_3$ did not interfere with the precipitation of orthophosphate at 12 mg/ℓ P when a reactant equivalence ratio of 1.0 was used. The orthophosphate-Fe(II) reaction in a wastewater (secondary effluent) environment was similar to that for pure orthophosphate solution and for orthophosphate solution containing bicarbonate alkalinity.

(f) On an equivalence basis, pyro- and tripolyphosphates are less effectively precipitated with ferrous iron than orthophosphate. For a phosphate concentration of 1.16×10^{-3} eq/ℓ, an initial pH of 8.0 and a reactant equivalence ratio of 1, maximum phosphate and iron removals were, respectively, 94 and 97% for orthophosphate, 87 and 91% for pyrophosphate and 11 and 12% for tripolyphosphate.

(g) In all experiments any precipitates retained on the membrane filters were initially light to dark green in color. On exposure to air all precipitates changed color, turning yellow or blue depending on pH and reaction time. The blue precipitate obtained in one orthophosphate precipitation at the optimum pH was examined by x-ray diffraction and identified as vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$.

(h) Comparison of the orthophosphate precipitation data for Fe(II) with the published data for Fe(III) and Al(III) indicates that the pH of optimum orthophosphate removal is higher for Fe(II) than for Fe(III) or Al(III) (~ 8.0 vs. ~ 3.5 for Fe(III) and ~ 5 for Al(III)) and that at the respective pH of optimum orthophosphate removal, the equivalence

capacity of Fe(II) for phosphate removal is higher than those for Fe(III) and Al(III).

(i) The pH-dependence of orthophosphate removal efficiency for Fe(II), Fe(III) and Al(III) and the higher equivalence capacity of Fe(II) for orthophosphate removal are in reasonable accord with a phosphate precipitation model in which hydroxide and orthophosphate ions compete for reaction with the cation.

In wastewater treatment with Fe(II) in the presence of dissolved oxygen, the phosphate precipitation system becomes complicated by the generation and subsequent hydrolysis of Fe(III) and in this regard the system differs from phosphate precipitation with pure Fe(III) and with Fe(II) in the absence of dissolved oxygen. For a given quantity (weight) of iron used, phosphate removal efficiency is higher for Fe(II) than for Fe(III) from a stock source when Fe(II) is completely oxidized in situ resulting in homogeneous generation of Fe(III).

In general, the precipitates formed in the treatment of secondary effluent with Fe(II) in the presence of dissolved oxygen were very fine and did not settle well. The settling properties of the precipitates formed with Fe(III) and Al(III) were superior to those obtained with Fe(II).

A program is recommended to investigate a process for the removal of phosphates from wastewater using ferrous iron under oxidizing conditions with the aim of process optimization. In this process, ferrous salt, such as waste pickle liquor from steel mills (an inexpensive source of Fe(II) in some large metropolitan areas) is added to the raw or settled sewage with the result that significant phosphate removal is effected. Subsequent aeration of the wastewater in an activated sludge tank should result in the oxidation of residual ferrous iron, further precipitation of phosphate, partial removal of organics and improvement in the sludge characteristics. Such a process promises to be more economical than other precipitation techniques.

SECTION II

RECOMMENDATIONS

The basic objective of the study described in this report has been to obtain some fundamental data which heretofore had been lacking on the orthophosphate-Fe(II) reactions. Most of the precipitation studies were conducted on pure phosphate solutions and in the absence of dissolved oxygen. It should be pointed out that the study of cation-phosphate reaction in pure systems is an essential prerequisite to understanding the phosphate removal process from such complex and variable systems as domestic wastewater. With the results of this study as the background it is now possible to extend the work to an evaluation of the parameters which influence process efficiency with the specific objective of developing design criteria for wastewater treatment with Fe(II). The following areas of research are recommended as a logical extension of the present study. Although pure solutions of orthophosphate and secondary effluent may be used in a limited number of tests, the majority of the experiments should be conducted on raw and settled sewage under conditions similar to those encountered in large-scale applications.

(a) Evaluation of the effects of pH, Fe(II) dosage, dissolved oxygen level, and concentration of organic material (e.g., COD or TOC) on the rate of oxidation of Fe(II) and on the efficiency of phosphate and organic removal. (The chemical treatment of wastewaters for the purpose of phosphate removal invariably results in some removal of dissolved and colloidal organic matter. The degree of organic removal associated with phosphate precipitation is an essential consideration in evaluating the process ecoromics.)

(b) Determination of the nature and extent of particle charge and their relations to such precipitate characteristics as settleability and filterability as a function of the wastewater parameters mentioned in (a) above. These precipitate properties are of major practical concern in the design and operation of solids-liquid separation units. Any improvements in these properties without the addition of poly-electrolytes results in a saving in the operating cost. In evaluating the effect of pH on particle charge and precipitate characteristics, both sodium hydroxide and lime should be used for pH adjustment and the results compared.

(c) Evaluation of the effect of aeration or addition of ozone or chlorine compounds on the rate of in situ oxidation of ferrous iron and on the efficiency of phosphate and organic removal. In a number of aeration

Preceding page blank

tests, conditions should be selected to simulate those existing in the activated sludge aeration tank and data should be collected on the settleability of the chemical-biological flocs.

(d) Comparison of the effectiveness of ferrous salts and waste pickle liquors for wastewater treatment using both sulfuric acid and hydrochloric acid pickling wastes. Waste pickle liquor contains mineral acidity which may lower the pH of the wastewater thus necessitating supplementary pH adjustment by addition of base.

(e) Evaluation of the use of Al(III), Fe(III), and polyelectrolytes in conjunction with Fe(II) for improving the characteristics of the precipitates formed in wastewater treatment with Fe(II). When used from a stock source, Al(III) and Fe(III) hydrolyze in solution to a considerable extent. Hydrolysis products of Al(III) and Fe(III), because of their gelatinous nature, may serve as flocculant aids thus improving the precipitate settleability.

(f) Characterization of the sludge produced in the treatment of wastewater with Fe(II). This should include water content, compactibility, and dewaterability. These sludge characteristics are important parameters in determining the costs of sludge handling and disposal.

(g) A preliminary economic assessment of large-scale wastewater treatment using Fe(II).

SECTION III

INTRODUCTION

Even with the advent of phosphate-free detergents, the removal of phosphates from wastewaters is regarded as essential for the control of eutrophication and prevention of water quality deterioration in many receiving streams. Of a number of methods available for phosphate removal, chemical precipitation (often called coagulation) using aluminum, ferric iron, ferrous iron and lime is considered to be the most economical.[1, 2] The chemistry of phosphate precipitation with aluminum, ferric iron and lime has been the subject of several research studies[3, 4] and, accordingly, the optimum conditions for phosphate removal with these salts are fairly well defined.

Although ferrous iron has been utilized for the removal of phosphates in some large-scale applications,[2] the fundamental aqueous chemistry of phosphate-Fe(II) reactions appears to be almost totally unexplored. No mention of exclusion of dissolved oxygen is made in all the reported laboratory evaluation tests with Fe(II). Since partial or total oxidation of Fe(II) to Fe(III) is almost inevitable in the presence of dissolved oxygen, the reported data cannot be regarded as true representation of reactions in the Fe(II)-orthophosphate system. From the standpoint of treatment cost, the use of ferrous iron for phosphate removal is economically appealing since in certain areas of the country waste pickle liquor from local steel industries may provide an inexpensive source of ferrous iron.

The objective of the present study has been two-fold: (a) to evaluate the effects of pH and reactant concentration on the rate and efficiency of phosphate removal from synthetic and secondary effluent wastewaters and on the nature of the precipitates formed, and (b) to compare the data on the Fe(II)-phosphate precipitation system with the available data for Fe(III)- and Al(III)-phosphate systems. In order to obtain for the first time the fundamental data on the orthophosphate-Fe(II) reaction, most of the experiments in this study were conducted on pure orthophosphate solutions and in the absence of dissolved oxygen (to prevent oxidation of ferrous iron to ferric iron). Only a limited number of tests were made of the use of ferrous iron for orthophosphate removal from wastewaters containing dissolved oxygen.

SECTION IV

EXPERIMENTAL

This section describes the materials, apparatus, and the general procedures used in this investigation. Special methods and modifications are described in the Results section, when appropriate.

Materials

Reagent grade sodium monohydrogen (ortho-) phosphate (Na_2HPO_4) tetrasodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$), sodium tripolyphosphate ($Na_5P_3O_{10}$), sodium bicarbonate ($NaHCO_3$), ferrous ammonium sulfate [$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$], ferrous perchlorate [$Fe(ClO_4)_2 \cdot 6H_2O$], ferric ammonium sulfate [$FeNH_4(SO_4)_2 \cdot 12H_2O$], and aluminum sulfate [$Al_2(SO_4)_3 \cdot 18H_2O$] were used to prepare the test solutions. All Fe(II), Fe(III) and Al(III) solutions were prepared fresh in concentrated form immediately before use. Doubly distilled water was used in the preparation of all test and reagent solutions. The doubly distilled water used in experiments with Fe(II) was degasified by boiling. It was then cooled and purged with either argon or nitrogen gas prior to use.

The orthophosphate solution used in most experiments contained 12 mg/ℓ P orthophosphate (1.16×10^{-3} eq/ℓ PO_4^{-3} or 3.87×10^{-4} M). This concentration was selected as representative of that to be encountered in a high phosphate secondary effluent and because the precipitation of phosphate at this level with Al(III) and Fe(III) had been extensively studied in a previous investigation.[4] An 18 mg/ℓ P solution of tetrasodium pyrophosphate (1.16×10^{-3} eq/ℓ $P_2O_7^{-4}$) and a 21.6 mg/ℓ P solution of sodium tripolyphosphate (1.16×10^{-3} eq/ℓ $P_3O_{10}^{-5}$) were used in the experiments with condensed phosphates.

The wastewaters (secondary effluent) used in phosphate precipitation studies were obtained from the Tapia Park Treatment Plant of the Las Virgenes Municipal Water District in Calabasas, California. This treatment plant is a small (~ 2 mgd) activated sludge plant which serves a primarily residential community. The plant is currently being expanded and during the months when samples were collected it was not always operating at a high efficiency, as evidenced by the high concentrations of phosphate and turbidity in the plant effluent (see Table 1). Partial analyses of the wastewater samples used in this study are given in Table 1. With the exception of Wastewater #2, which was not filtered, all samples were filtered through Whatman #1 paper prior to use in phosphate precipitation tests.

Preceding page blank

TABLE 1

PARTIAL ANALYSES OF THE SECONDARY EFFLUENT SAMPLES USED IN VARIOUS PRECIPITATION EXPERIMENTS[a]

Constituents	Wastewater #1	Wastewater #2	Wastewater #3	Wastewater #4	Wastewater #5
pH	7.25	7.35	7.32	7.51	7.51
Temperature (°C)	22.2	19.5	23.0	19.5	18.0
Conductivity (at above temperature) (mmho)	1.75	1.75	1.82	1.80	1.70
Alkalinity (mg/ℓ $CaCO_3$)	330	557	530	586	553
Turbidity (JTU)	4.3	7.5	5.0	15	8
Orthophosphate[b] (mg/ℓ P)	15.8	9.1	18.3	11.2	9.0
Date Collected	10-27-70	12-18-70	10-19-70	12-14-70	1-12-71

[a]Data are for the wastewater as received in the laboratory and prior to filtration through Whatman #1 paper.

[b]Orthophosphate determinations made on Whatman #42 filtrates.

Apparatus

Commercial Items. Radiometer PHM 26 and PHM 28 pH meters were used for pH measurements. All conductivity determinations were made with a Radiometer Model CDM2e conductivity meter. A Radiometer automatic titration control unit, Type TTT 11 was used in conjunction with Radiometer PHM 26 pH meter for the constant pH precipitation experiments. A Hewlett-Packard/Moseley Model 7100 B two-pen strip chart recorder was used for recording pH. All turbidity measurements were made with a Hach Laboratory Turbidimeter Model 2100. The colorimetric analyses were made with a Beckman DB-G Grating

Spectrophotometer. The x-ray diffraction analyses were made on a Norelco 50 KV diffractometer. All "jar test" precipitation experiments were conducted using a Phipps and Bird six-place stirrer.

Controlled Atmosphere Reaction System. The ferrous iron in an aqueous solution is subject to oxidation by the dissolved oxygen. To minimize the oxidation of ferrous iron during the precipitation experiments, a special system was constructed which permitted the experiments to be conducted under an oxygen-free argon atmosphere. The schematic diagram and a photograph of the system are shown in Figures 1 and 2, respectively. The heart of the system is a special thermostatted reaction unit fitted with a #13 rubber stopper containing openings for the support of pH electrodes, thermometer, and gas inlet tubes, and for the addition of reagents, withdrawal of the samples, and gas exit. This last opening is kept plugged except during reagent addition or sample withdrawal. The reaction vessel which fits into a 6 in. x 6 in. x 6-3/4 in. Plexiglas water bath is a 2-ℓ Pyrex beaker with its tip rounded to fit into a 1/4 in. deep circular groove cut into the 1/2 in. thick Plexiglas cover. To provide a tight seal, the groove is partially filled with Apiezon Q Sealing Compound. The Plexiglas cover plate also has a 2-1/2 in. diameter hole at its center which accommodates the #13 rubber stopper containing the pH electrodes, etc. Mixing and agitation in the reaction vessel are provided by means of a magnetic stirrer. The reaction vessel can be purged through either of the two gas inlet tubes. One tube extends to within 1/2 in. of the bottom of the beaker; the second tube extends only to a level just above the water surface. The argon gas used for purging passes through a hot copper oxygen removal unit, and a humidifier prior to entrance into the reaction vessel.

To prevent air oxidation of Fe(II) to Fe(III) during filtration, a special vacuum filtration apparatus was constructed and used which allowed for operation under an inert gas atmosphere. The apparatus consisted of a standard Millipore filtration unit with the sample holder converted to a covered chamber with two openings: one for gas inlet and another for sample introduction and gas exit. The collection flask is a regular vacuum flask which is connected to a vacuum source.

System for Settling Rate Studies. Figure 3 is a photograph of the system used for the measurement of the settling rates of the chemical flocs produced in phosphate removal from wastewater using Fe(II), Al(III), and Fe(III) salts. The design of this system is essentially the same as that recommended by Cohen.[5] The system consists of a Phipps and Bird six-place stirrer (for mixing and flocculation for a short period after the addition of coagulants) and a special apparatus which permits

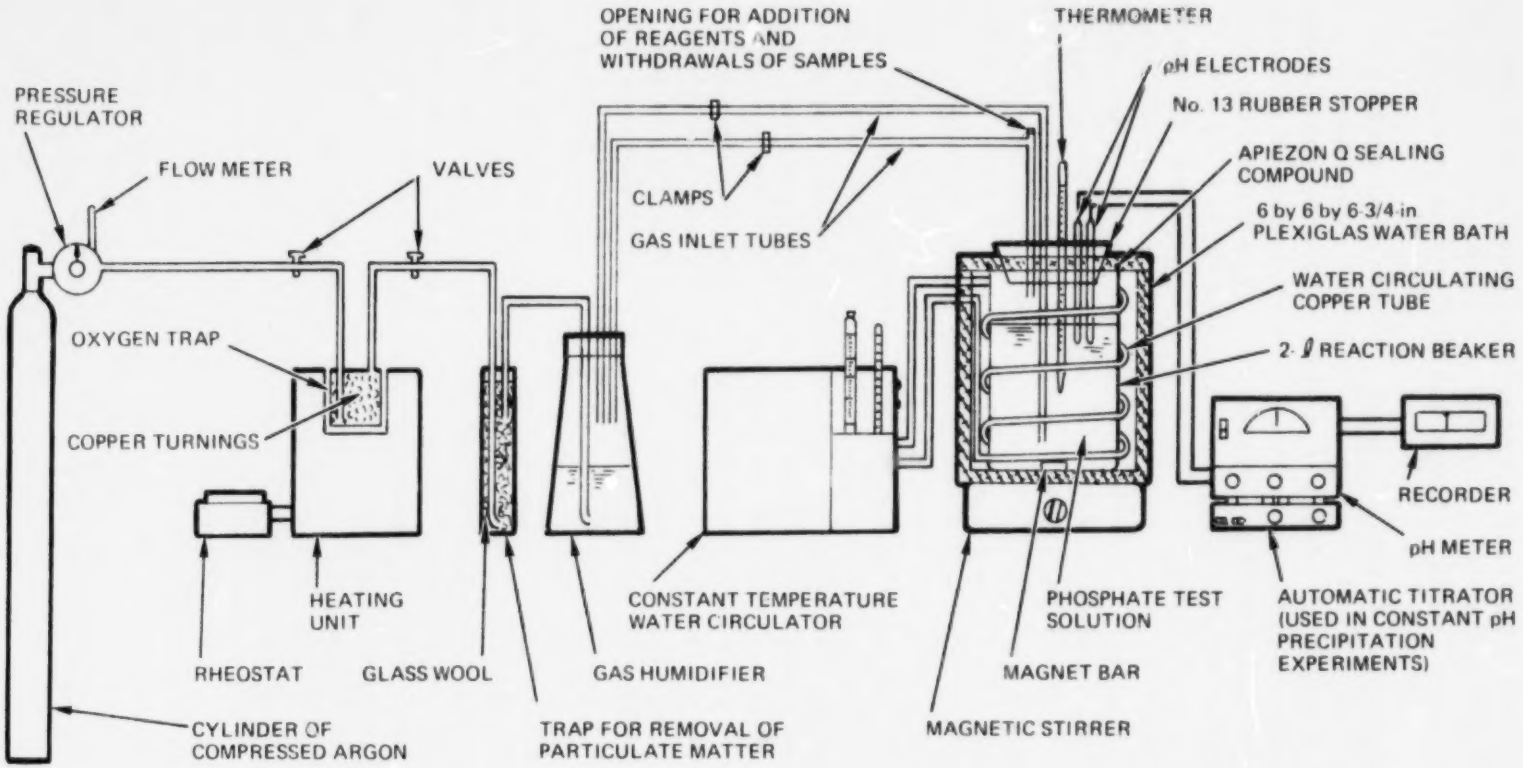


FIGURE 1. SCHEMATIC DIAGRAM OF THE CONTROLLED ATMOSPHERE REACTION SYSTEM

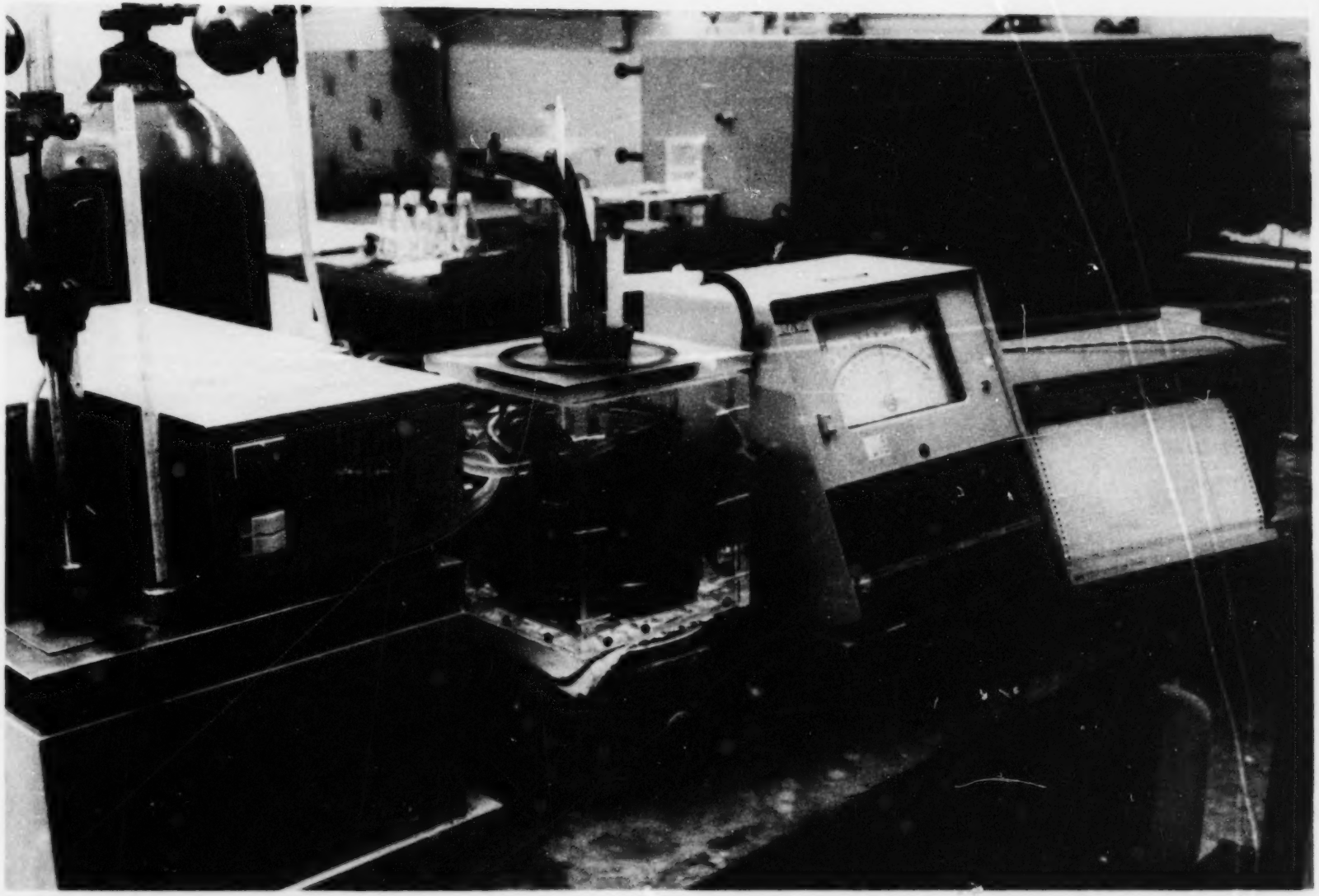


Figure 2. Controlled Atmosphere Reaction System

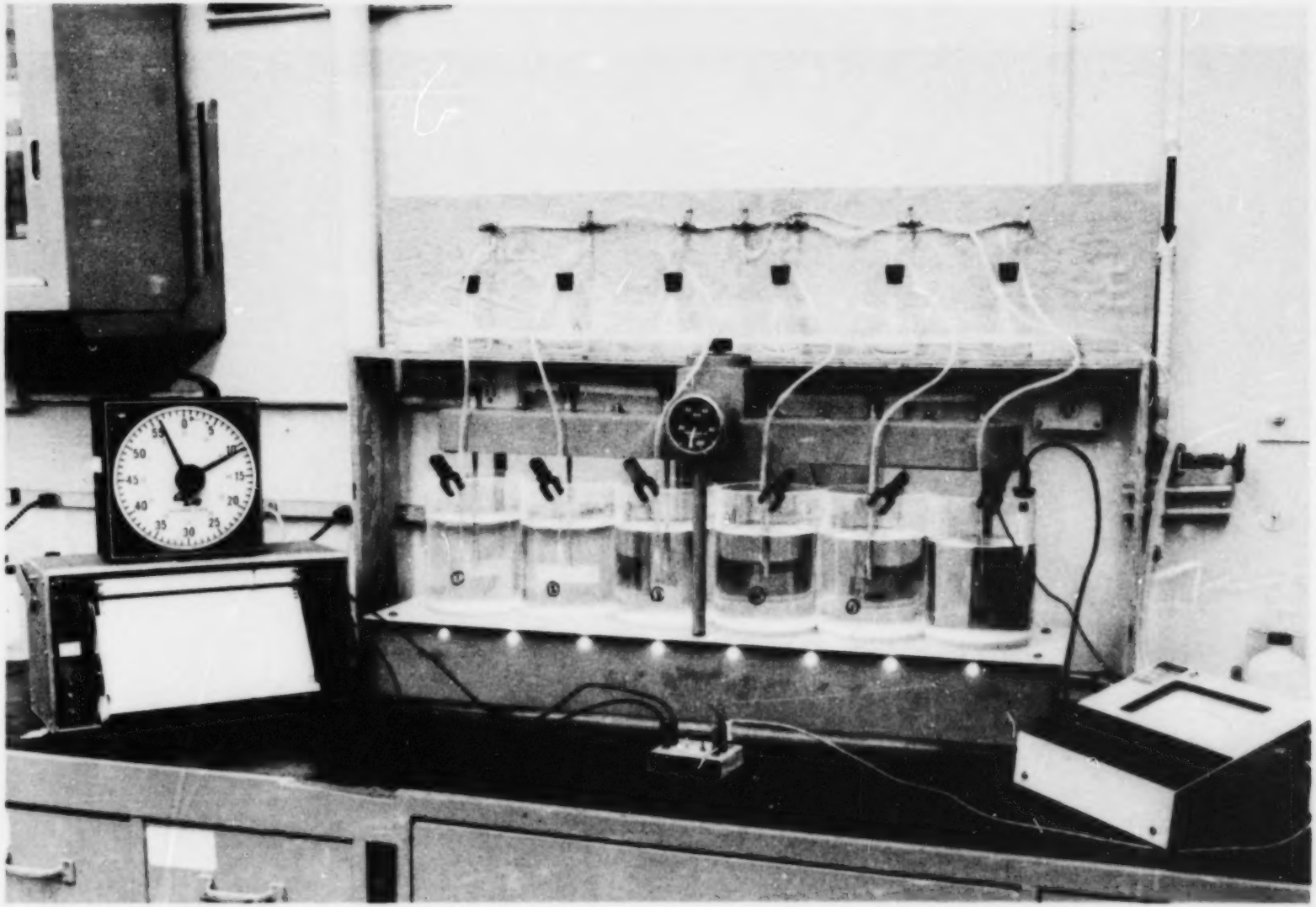


Figure 3. System for Settling Rate Studies

automatic and periodic withdrawal of sample aliquots at any pre-selected distance below the water surface for the purpose of turbidity and/or chemical analysis. The sampling containers are 125-ml Erlenmeyer flasks, individually connected to a vacuum manifold through small needle valves. The sampling tubes are 3/32-in. ID stainless steel which are connected to the Erlenmeyer flasks by 1/8 in. ID Tygon tubes. The "on-off" control for the vacuum to the system is a plastic "T" which is open to the atmosphere at one end and is connected to the vacuum manifold and a vacuum source at the other ends. By closing the open end of the "T" the vacuum is diverted to the manifold and the water from each jar flows into the sampling containers. The needle valves were adjusted so that the rates of flow were nearly the same for all six sampling units and that a sample of 20 to 25 ml volume could be collected in each flask when the vacuum was applied to the manifold for a period of 4 to 5 seconds. In operation, following the collection of each set of samples, the sampling flasks are replaced with empty containers for subsequent sampling.

Analytical Procedures

All phosphate and iron analyses were performed in accordance with the procedures described in ASTM Manual on Industrial Water and Industrial Waste Water.[6] The colorimetric amino reduction method with bismuth modification (ASTM Designation D515-66T) was used for orthophosphate determination. The polyphosphates were analyzed by hydrolyzing them to orthophosphate by boiling with acid and then determining them as orthophosphates. Ferrous and total iron analyses were carried out by the orthophenanthroline colorimetric method (ASTM Designation D1068-62T, Referee Method A).

Experimental Procedures

Experiments Using the Controlled Atmosphere Reaction System. The Controlled Atmosphere Reaction System (described above) was used to carry out the phosphate precipitation experiments in the absence of dissolved oxygen. The procedure in these tests was as follows. Fifteen hundred ml of the test phosphate solution was placed in the reaction vessel and purged with argon (through the lower gas inlet within the solution) for about 45 to 60 min. Then, while the phosphate solution was being rapidly mixed with a magnetic stirrer, 5 to 10 ml of an Fe(II) solution of appropriate concentration was added from a pipette to the solution to establish the desired Fe(II)-to-phosphate equivalence ratio. After the addition of Fe(II) and during the course of the precipitation, the argon was passed to the system either through the lower gas inlet located in the solution or through the gas inlet located above the solution surface. All experiments were conducted

at 25.0°C. Two methods of pH adjustment were employed. In a few experiments, NaOH (0.1 N) was added to the test solution prior to the addition of Fe(II). In other tests, a Radiometer Automatic Titrator was employed to control the pH during and for a short period (see below) after the addition of Fe(II) through automatic addition of NaOH.

A detailed description of the operating principle of the Radiometer Titrator is available elsewhere.[7] In short, the titrator compares the meter reading of the pH meter with a current which represents the desired final pH. The difference between the two currents (termed the "error" current) is amplified and applied to a switch circuit which energizes an electromagnetic valve. The valve is used to control the titrant (NaOH in this study) flow from a burette. The design of the titrator provides for an average flow to the sample which is proportional to the error current within a certain manually selected range called the proportional band. Within the proportional band the titrant is added to the sample in increments because the valve has only two positions, closed or open. The proportional reduction of the average flow is accomplished automatically by a continuous reduction of the increments and a continuous increase of the interval between two increments.

In the experiments where the titrator was used for pH control, because of the operating principle of the titrator and because of the nature of the precipitation reactions, a final pH close to the desired level could not be attained by the time all the Fe(II) had been delivered to the reaction beaker (the addition of Fe(II) generally lasted about 1 min). Accordingly, in the precipitation tests the pH adjustment was allowed to continue for up to 4.0 min after the start of Fe(II) addition. With this procedure, the final pH at the termination of pH adjustment was usually within 0.1 pH unit of the desired level.

For 5 hours after the addition of Fe(II), and while the solution was continuously being stirred, aliquot samples of the reaction mixture were removed from the reaction vessel at selected time intervals and analyzed for turbidity or soluble residual reactant concentrations. The sampling technique is demonstrated in Figure 4. The aliquots removed for chemical analysis (40 ml each) were filtered through 100 mμ Millipore membrane filters. The filtration was performed under nitrogen or argon in the special filtration unit described above under "Apparatus". (The nitrogen gas used was not pretreated to remove the traces of oxygen which might have been present.) To retard the oxidation of Fe(II) to Fe(III) in the filtrate, 1 ml 1 N HCl was placed in the collection flask. (In the polyphosphate experiments and in the experiment with wastewater, 1 ml concentrated HCl was used in place of 1 ml 1 N HCl to assure a sufficiently low pH.) In all experiments the test solution

Figure 4. Sample Removal from Reaction Vessel

was visually observed for turbidity formation. In a few experiments turbidity was quantitatively determined on sample aliquots (25 ml) removed specifically for this purpose. In all experiments the solution pH was continuously monitored during the course of the precipitation.

The precipitates retained on the membrane filters were observed for color characteristics before and following exposure to air. In some cases, the exposed precipitates (retained on the membranes) were examined by powder x-ray diffraction for crystallinity and chemical nature.

Precipitation Experiments with Fe(II) in the Presence of Dissolved Oxygen. The effect of dissolved oxygen on phosphate removal with Fe(II) was evaluated in three experiments in which no measures were taken to remove oxygen from the phosphate test solution. A 12 mg/ℓ P orthophosphate solution containing 420 mg/ℓ $NaHCO_3$ was used in one of the experiments conducted at 25.0°C in the thermostatted reaction vessel shown in Figure 1. An Fe(II)-to-orthophosphate equivalence ratio of 1.0 was used in this test. The other two experiments were conducted on an unfiltered wastewater (Wastewater #2, Table 1) using Fe(II)-to-orthophosphate equivalence ratios of 0.5 and 1.5. These tests were performed at room temperature (25 ± 2°C) with mixing and flocculation provided by a Phipps and Bird six-place stirrer. The mixing and flocculation consisted of 2 min rapid mixing at 90 rpm followed by one hour of slow mixing at 20 rpm. After 1 hr of quiescent settling, aliquots were filtered through 100 mμ Millipore membrane filters and the filtrates analyzed for phosphate and total iron. Other experiments conducted with Fe(II) in the presence of dissolved oxygen are described in the next section where the procedures used for the settling rate studies are described.

Settling Rate Studies. The system for settling rate studies (described earlier under "Apparatus" section) was used for the evaluation of the effect of Fe(II) dose (actually Fe(II)-to-orthophosphate equivalence ratio) on the formation and settling characteristics of the precipitates formed in the treatment of secondary effluent with Fe(II). The experiments were conducted on 1.5-ℓ samples of a filtered secondary effluent (Wastewater #3, Table 1) using Fe(II)-to-orthophosphate equivalence ratios of 0.4, 0.8, 1.2, 1.5, and 2.0. Following mixing and flocculation (2 min rapid mixing at 90 rpm, 10 min slow mixing at 20 rpm), the precipitates were allowed to settle. The automatic sampler was used to obtain 20 to 25 ml sample aliquots from a position about 2.5 in. below the water surface after 2 min, 5 min, 15 min, 1 hr, and 2 hr of quiescent settling. The aliquots were thoroughly mixed and their turbidities determined immediately. The 2-hr aliquots were subsequently analyzed for orthophosphate content.

For comparison with the results of Fe(II) experiments, settling rate studies were also made of phosphate precipitates obtained with Fe(III) and Al(III). Wastewaters #4 and #5 (Table 1) were used in the experiments with Al(III) and Fe(III), respectively. In these experiments, at the end of 2 hr of settling, an aliquot from each solution was filtered through Whatman #42 paper. The filtrates were analyzed for orthophosphate content.

SECTION V

RESULTS AND DISCUSSION

Table 2 is a summary of the conditions used for 38 representative experiments. The results of these experiments are presented in Tables 3 through 17 and are discussed in detail in the text.

Precipitation Experiments with Fe(II) in the Absence of Dissolved Oxygen

Experiments with Pure Orthophosphate Solutions (Experiments 1-13)

Effect of pH on Turbidity Formation (Experiments 1-5). In the initial precipitation experiments with Fe(II), only the solution pH and turbidity were monitored. Table 3 gives the results of three experiments (Experiments 1-3) conducted with orthophosphate solutions initially at pH levels of 5.0, 7.0 and 9.0, with no subsequent pH adjustments during the addition of Fe(II) or after. As indicated by the data in this table, the solution pH in these experiments dropped immediately upon the addition of Fe(II), reaching values of 4.87, 6.77 and 7.32 within 2 min, respectively. In Experiment 1, it may be noted that no significant amount of turbidity was formed and no further change in pH occurred during the 6.0 hr observation period. In Experiment 2, the pH remained at 6.77 for the first 1 to 1-1/2 hr and then gradually dropped, reaching 6.50 at the end of 2 hr and an apparently constant value of 6.4 at the end of 2-1/2 hr. Turbidity formation was significant only after 1 to 1-1/2 hr. In Experiment 3, the initial pH remained constant for a shorter period of time (approximately 12 min) before it gradually decreased to a final value of 6.4. Also, the increase in turbidity over its initial value was more rapid in this test (30 min vs 1-1/2 hr in Exp. 2).

From the results of Experiments 2 and 3, it became evident that a study of the Fe(II)-orthophosphate reaction at a near constant high pH would require supplementary addition of a base during and subsequent to the addition of Fe(II). Table 4 shows the data obtained in two experiments (Experiments 4 and 5) in which the pH was maintained constant at 8.0 and 9.0, respectively, during the addition of Fe(II). In Experiment 4, the pH remained at 8.0 for about 2 min after Fe(II) addition and discontinuation of pH control. It then gradually decreased, reaching 7.60 after 2 hr and 7.51 after 5 hr. The turbidity content of the product solution increased with the drop in pH, reaching a maximum value of 48 JTU after 1-1/2 hr, and remained constant thereafter. At pH 9.0 (Experiment 5) the precipitate formation was more rapid and the

Preceding page blank

TABLE 2

SUMMARY OF EXPERIMENTS DISCUSSED IN TEXT

	Exp. No.	Initial pH	Initial Phosphate Concentration (mg/ℓ P)	Cation-to-Phosphate Equivalence Ratio	Parameters Measured or Observed[a]	Table(s) Containing Results
I. Experiments with Fe(II) in the absence of dissolved oxygen						
A. Tests with pure orthophosphate solutions						
1. Effect of pH on precipitate formation	1-5	5.0-9.0	12	1.0	pH, TF	3, 4
2. Effect of pH on speed and efficiency of reaction	6-10	6.0-10.0	12	1.0	pH, RRC, PC, PCN	5
3. Effect of reactant concentration on speed and efficiency of reaction	11-13	7.9	12, 4	1.0, 1.5, 0.33	pH, PC, RRC (Exp. 11 only)	6, 7
B. Test with orthophosphate solution containing 420 mg/ℓ $NaHCO_3$	14	7.9	12	1.0	pH, RRC, PC	8
C. Test with secondary effluent (Wastewater #1, Table 1)	15	7.4	15.8	1.5	pH, RRC, PC	9
D. Test with pyro- and tripolyphosphate	16, 17	7.9	18(pyro-) 21.6(tripoly-)	1.0	pH, RRC, PC	10
II. Experiments with Fe(II) in the presence of dissolved oxygen						
A. Test with orthophosphate solution containing 420 mg/ℓ $NaHCO_3$	18	7.2	12	1.0	pH, RRC, PC	12
B. Test with secondary effluent (Wastewater #2, Table 1)	19, 20	7.5, 7.4	9.1	0.5, 1.0	pH, RRC, PC	13
C. Settling rate studies with secondary effluent (Wastewater #3, Table 1)	21-26	-	18.3	0.4-2.0	pH, TF, SR, RRC	14, 15
III. Settling rate studies with Fe(III) and Al(III) on secondary effluent						
A. Experiments with Al(III) (Wastewater #4, Table 1)	27-32	-	11.2	0.4-2.0	pH, TF, SR, RRC	16
B. Experiments with Fe(III) (Wastewater #3, Table 1)	33-38	-	9.0	0.4-2.0	pH, TF SR, RRC	17

[a]Abbreviations: TF = Turbidity Formation, RRC = Residual Reactant Concentration, PC = Precipitate Color, PCN = Precipitate Chemical Nature, SR = Settling Rate

TABLE 3

CHANGES IN SOLUTION TURBIDITY AND pH IN ORTHOPHOSPHATE PRECIPITATION WITH Fe(II)[a, b]

Time After Addition of Fe(II)	Experiment 1 (Initial pH = 5.0)		Experiment 2 (Initial pH = 7.0)		Experiment 3 (Initial pH = 9.0)	
	pH	Turbidity (JTU)	pH	Turbidity (JTU)	pH	Turbidity (JTU)
2 min	4.87	-[c]	6.77	-	7.32	-
5 min	4.87	0.23	6.77	0.8	7.32	15
15 min	4.86	0.22	6.77	1.2	7.21	16
30 min	4.87	0.24	6.77	1.3	6.82	24
1 hr	4.87	0.23	6.78	1.3	6.58	29
1-1/2 hr	4.88	0.30	6.72	4.0	6.50	30
2 hr	4.89	0.35	6.50	7.0	6.48	28
3 hr	4.90	0.27	6.40	8.5	6.43	29
4 hr	4.91	0.24	6.40	8.4	6.41	-
5 hr	4.93	0.26	6.40	8.7	6.40	29
6 hr	4.93	0.32	-	-	-	-

[a] No pH adjustment during or after addition of Fe(II)

[b] Initial orthophosphate concentration = 12 mg/ℓ P; Fe(II)-to-orthophosphate equivalence ratio = 1.0

[c] - indicates no measurements were made

TABLE 4

CHANGES IN SOLUTION TURBIDITY AND pH IN ORTHOPHOSPHATE PRECIPITATION WITH Fe(II)[a, b]

Time After Addition of Fe(II)	Experiment 4 (Initial pH = 8.0)		Experiment 5 (Initial pH = 9.0)	
	pH	Turbidity (JTU)	pH	Turbidity (JTU)
2 min	8.00	-[c]	9.0	-
5 min	7.98	20	9.0	13
15 min	7.95	20	9.0	13
30 min	7.86	26	9.0	13
1 hr	7.72	42	9.0	12
1-1/2 hr	7.65	48	9.0	12
2 hr	7.60	48	9.0	11
3 hr	7.58	47	9.0	12
4 hr	7.53	48	9.0	13
5 hr	7.51	48	9.0	15

[a] pH continuously kept adjusted to initial value during addition of Fe(II) which lasted 30 to 60 sec

[b] Orthophosphate concentration = 12 mg/ℓ P; Fe(II)-to-orthophosphate equivalence ratio = 1.0

[c] - indicates no measurements made

precipitates were larger in size than in Experiment 4. No change in solution pH occurred subsequent to addition of the Fe(II) in this experiment and turbidity remained constant after the initial reactions.

As will be seen later, the observed changes in pH and turbidity of the product solutions correspond to changes in the concentration of residual soluble reactants. If the overall precipitation reaction is represented by $3Fe^{+2} + 2H_2PO_4^- \text{ (or } 2HPO_4^{-2}) = Fe_3(PO_4)_2 + 4H^+ \text{ (or } 2H^+)$, the release of protons from such a reaction can account for the observed decrease in the pH. The data in Tables 3 and 4 indicate that the rate of precipitation of orthophosphate with Fe(II) in the pH 5 to 8 region is pH dependent, increasing with a rise in pH. As will be discussed later, the formation of turbidity at pH 9.0 is due to the precipitation of the excess iron as hydroxide in addition to precipitation of ferrous phosphate.

Effect of pH on Rate and Efficiency of Reactant Removal (Experiments 6-10). Table 5 contains data on changes in solution pH and residual reactant concentrations for a reaction time of 5 hr for five experiments (Experiments 6 through 10) conducted at initial pH levels of 6.0, 7.0, 7.9, 8.9, and 10.0. In Experiments 6, 7, and 9 the turbidity of the product solution was also measured at the termination of the experiments (after 5 hr). The following is a discussion of results for the individual experiments.

In Experiment 6 (initial pH = 6.0) the changes in pH and reactant concentrations were fairly small. The total drop in pH and orthophosphate and ferrous iron concentrations were 0.2 pH unit, and 7 and 9%, respectively. The turbidity of the reacted mixture after 5 hr was only 4 JTU in this experiment.

In Experiment 7, the solution pH remained constant at 7.0 for about 20 sec following the termination of pH adjustment and then dropped to the various levels indicated in Table 5. Most of the change in solution pH occurred during the second half of the first hour. This decrease in the pH was accompanied by a significant decrease in residual reactant concentrations. The orthophosphate and ferrous iron removals remained essentially constant after the second hour with maximum removal levels of 35 and 39%, respectively. In this experiment, the turbidity of the solution mixture at the end of the 5 hr was 22 JTU.

The solution pH in Experiment 8 was 7.90 at the termination of pH adjustments and 7.89 at the end of 5 min. After 5 min, the solution pH decreased slightly, reaching a minimum value of 7.82 by the end of

TABLE 5

EFFECT OF pH ON ORTHOPHOSPHATE PRECIPITATION WITH Fe(II)[a]

Time[b]	Experiment 6 (Initial pH = 6.0)			Experiment 7 (Initial pH = 7.0)			Experiment 8 (Initial pH = 7.9)			Experiment 9 (Initial pH = 8.9)			Experiment 10 (Initial pH = 10.0)		
	pH[c]	Percent Reactant Removal		pH[c]	Percent Reactant Removal		pH[c]	Percent Reactant Removal		pH[c]	Percent Reactant Removal		pH[c]	Percent Reactant Removal	
		P	Fe		P	Fe		P	Fe		P	Fe		P	Fe
5 min	5.95	-[d]	-	6.95	-	-	7.89	-	-	8.88	-	-	9.99	17	~100
15 min	5.90	7	8	6.87	17	24	7.88	62	78	8.88	69	≃100	9.98	13	~100
30 min	5.87	7	9	6.81	17	24	7.82	63	79	8.88	69	≃100	9.98	18	~100
1 hr	5.82	7	9	6.40	30	34	7.99	83	94	8.88	69	≃100	9.98	13	~100
2 hr	5.82	7	7	6.20	35	37	7.91	93	96	8.88	69	≃100	9.98	13	~100
3 hr	5.82	7	6	-	35	38	7.90	94	96	8.88	69	≃100	9.98	13	~100
4 hr	5.80	7	9	-	35	39	7.89	94	97	8.88	69	≃100	9.98	10	~100
5 hr	-	7	9	-	35	39	7.89	94	97	-	69	≃100	9.95	10	~100
Final Turbidity	4 JTU			22 JTU			-			35 JTU			-		

[a] Initial orthophosphate concentration = 12 mg/ℓ P; Fe(II)-to-orthophosphate equivalence ratio = 1.0

[b] Time from the start of Fe(II) addition and beginning of pH adjustment

[c] pH adjustment made initially by addition of 0.1 N NaOH concurrent with and for up to 4 min after the addition of Fe(II)

[d] - indicates no measurements were made

30 min. In the second half of the first hour the solution pH increased a total of 0.17 pH unit and then gradually decreased reaching its initial value of 7.89 by the end of 4 hr. To assure that the observed increase in solution pH was real and not an artifact, Experiment 8 was repeated several times. The pattern of change in pH was the same in all cases. The increase in solution pH was unique to Experiment 8 and was not observed in experiments conducted at other pH levels.

As with Experiment 7, a significant portion of the total reactant removal in Experiment 8 occurred in the second half of the first hour. The observed pattern of change in solution pH and the variation in the rates of orthophosphate and iron removal together with the data collected on precipitate characteristics (see discussion on precipitate characteristics) suggest that in the vicinity of pH 8.0 the mechanism by which reactants are removed from solution and the composition of the products formed vary with time. Although the exact mechanism(s) which results in a rise in solution pH is not known, the following types of reaction could account for the observed phenomenon:

$$Fe^{+2} + H_2O = Fe(OH)^{+} + H^{+}$$
$$H^{+} + OH^{-} = H_2O$$
$$Fe^{+2} + 2\,OH^{-} = Fe(OH)_2(s)$$

Reactions during initial pH adjustment

$$3Fe(OH)^{+} + 2HPO_4^{-2} \rightarrow Fe_3(PO_4)_2(s) + 2H_2O + OH^{-}$$
$$3Fe(OH)_2 + 2HPO_4^{-2} \rightarrow Fe_3(PO_4)_2(s) + 2H_2O + 4\,OH^{-}$$

Subsequent reactions

During the initial pH adjustment, some of the iron may form soluble hydroxy complexes or precipitates as hydroxide. Subsequent reaction of orthophosphate with ferrous hydroxide or ferrous hydroxy complexes results in the release of OH^{-} ion and thus a rise in pH (the last reactions).

In conjunction with Experiment 8, three side experiments were conducted to assess (a) the extent of oxidation of ferrous to ferric iron during the 5-hr precipitation test, (b) the effect of prolonged reaction time on the efficiency of phosphate removal, and (c) any release of phosphate from the precipitate when the reacted sample is exposed to air. Three 40-ml aliquots of the reaction mixture (designated as Samples A, B and C) were removed from the reaction beaker at the end

of 5 hours. Sample A was acidified with 1 ml N HCl and analyzed for both ferrous and total (ferrous plus ferric) iron content. The concentration of ferric iron in this sample was found to be less than 1 mg/ℓ which indicated that under the experimental conditions used the extent of oxidation of ferrous iron to ferric form was small (less than 3%). Samples B and C were not acidified. Sample B was thoroughly purged with argon and kept under an argon atmosphere. Sample C was not purged with argon and was left exposed to the laboratory atmosphere. On standing overnight the precipitate in flask C developed a blue color due apparently to partial oxidation of ferrous iron in the precipitate (see discussion on precipitate characteristics below). The precipitate in flask B retained its initial light green color. Both samples were filtered through 100 mμ membrane filters and the filtrates were analyzed for orthophosphate and residual iron content. No ferrous iron could be detected in either sample. The orthophosphate concentration was 0.81 mg/ℓ P for sample B and 1.09 mg/ℓ P for sample C (the orthophosphate residual measured at the end of 5 hr in Experiment 8 had been 0.71 mg/ℓ P). These results indicate that, for the conditions of Experiment 8, the partial oxidation of the ferrous iron in the precipitate to the ferric form only results in a small release of orthophosphate to solution, and that reaction times in excess of 5 hr will not result in an increase in orthophosphate removal. (Indeed, in both Experiments 7 and 8, most of the change in the residual reactant concentrations occurred within the first 2 hours.)

As indicated by the data in Table 5, in Experiment 9 there was no measurable change in solution pH or residual reactant concentrations with time. Large green precipitates (presumably containing $Fe(OH)_2$) were formed immediately after the addition of Fe(II). No iron could be detected in any of the filtrates. The maximum orthophosphate removal and the final turbidity of the product solution were 69% and 35 JTU, respectively. Except for less removal of the phosphate, the results of Experiment 10 were very similar to those of Experiment 9.

In summary, both the speed and efficiency of orthophosphate removal with Fe(II) are strongly pH dependent. The maximum orthophosphate removal efficiencies obtained in Experiments 6-10 are plotted in Figure 5 as a function of pH. (This figure also includes precipitation data for Fe(III) and Al(III) from Reference 4, which will be discussed later.) The pH for maximum orthophosphate removal is in the vicinity of 8.0 for Fe(II). In this study, no data were collected on orthophosphate precipitation at intermediate pH levels in the pH 7 to 8 and pH 8 to 9 regions to determine the exact pH of maximum orthophosphate removal. As will be discussed later, the observed pH dependency of

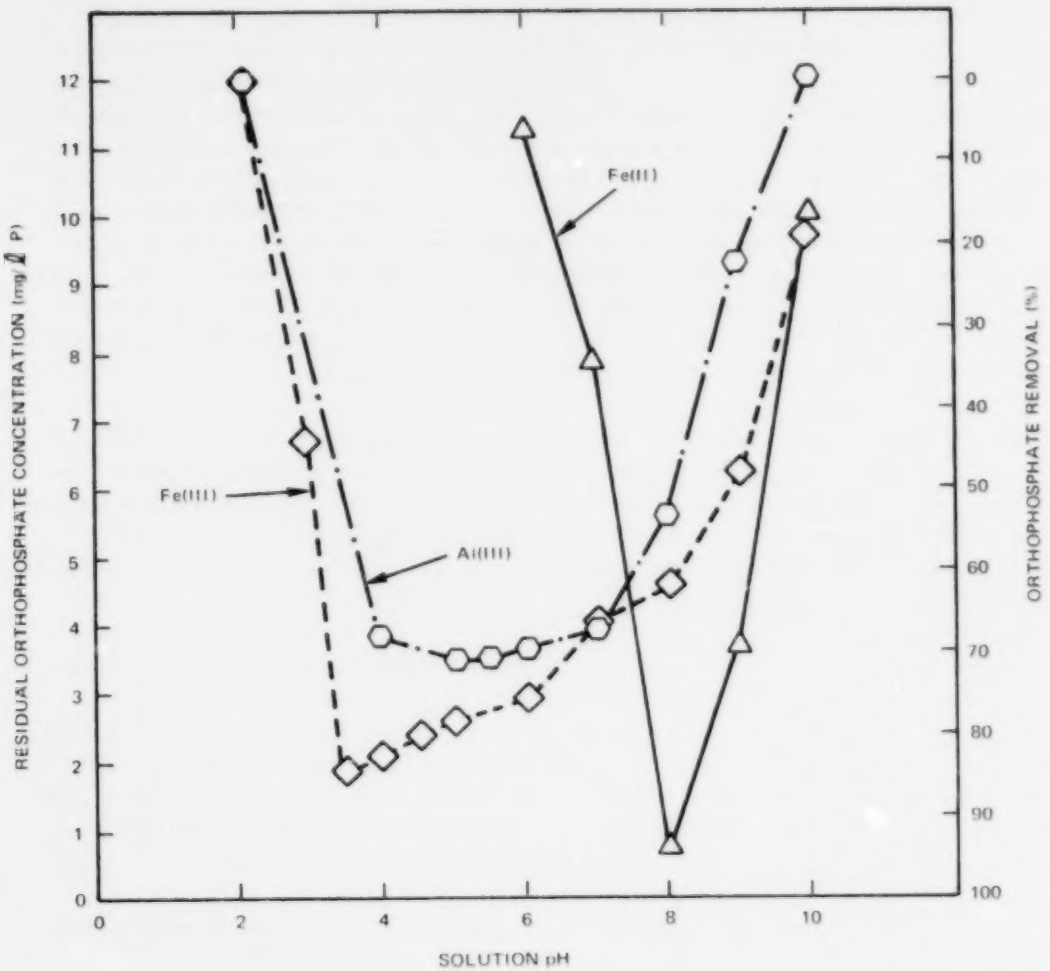


Figure 5. Precipitation of Orthophosphate with Fe(II), Al(III), and Fe(III) at a Cation-to-Orthophosphate Equivalence Ratio of 1.0

Initial Orthophosphate Concentration = 12 mg/ℓ P Na_2HPO_4

Residual Orthophosphate Determined on 100 mμ Membrane Filtrates

orthophosphate removal with Fe(II) can be explained in terms of a competition between hydroxide ion and orthophosphate ion to react with ferrous ion.

Precipitate Characteristics. The precipitates obtained in Experiments 6-10 were observed for color characteristics and some were also examined by the powder x-ray diffraction technique. In all cases the precipitates retained on 100 mμ membrane filters were initially light green at lower pH levels and darker green at higher pH levels. On exposure to air, however, all precipitates changed color. The precipitates from 15 min and 30 min samples in Experiments 7 and 8 (initial pH 7.0 and 7.9, respectively) and all precipitates from Experiments 6, 9 and 10 (initial pH 6.0, 8.9 and 10.0, respectively) turned yellow. The precipitates from the 1 to 5 hr samples in Experiment 7 developed a light blue-green color and those in Experiment 8 turned intensely blue. The yellow color was most intense in the precipitates from Experiments 9 and 10 and was barely visible in samples from Experiment 6. The 5 hr sample from Experiment 8 was initially blue but changed to green on vacuum drying (see below).

The development of the yellow color in the precipitates is believed to be due to the oxidation of ferrous iron by the atmospheric oxygen. In Experiment 9, following the termination of the experiment under argon atmosphere, the solution containing the precipitates was allowed to stand exposed to laboratory atmosphere. It, too, developed an intense yellow color on exposure to air.

The pattern of color change from green to blue-green or to intense blue has been reported to be a characteristic of the mineral vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$.[8] When freshly mined, vivianite is almost colorless (actually a very pale green) but develops a blue color on exposure to air. The change in color is attributed to the partial oxidation of Fe(II) to Fe(III). In Experiment 8, following the termination of the experiment, the solution containing the precipitate was exposed to air. On overnight standing, this precipitate also developed an intense blue color. The blue precipitate was collected by centrifugation and dried in a desiccator under vacuum at room temperature. The vacuum drying of the precipitate resulted in an irreversible change in the precipitate color from blue to green.

The vacuum dried precipitate and the materials from the 15 min and 5 hr samples dried in the laboratory atmosphere (also from Experiment 8) were examined by the powder x-ray diffraction technique. The 15 min sample was amorphous to x-rays but the 5 hr sample and the vacuum dried precipitates gave sharp diffraction patterns corresponding to that for vivianite. Since x-ray analysis was conducted under a vacuum

environment, the 5 hr precipitate, initially blue in color, developed a green color which did not revert to blue on subsequent exposure to air. No explanation can be offered for this color reversion.

The x-ray diffraction analysis results for the precipitates in Experiment 8, and the observed variation in the color of the precipitates in various experiments following exposure to air indicate that composition of the precipitate is affected by both the pH of the precipitation and by the reaction time.

Effect of Reactant Concentration on Reaction Speed and Efficiency of Reactant Removal (Experiments 11-13). Experiments 1 through 10 (Tables 3, 4 and 5) were all performed on 12 mg/ℓ P orthophosphate solutions using an Fe(II)-to-orthophosphate equivalence ratio of 1.0 (a ferrous iron dosage of 32.4 mg/ℓ). To assess the effect of reactant concentrations on the rate and efficiency of reactant removal, three other experiments (Experiments 11, 12 and 13) were conducted. Experiments 11 and 12 were conducted on 12 mg/ℓ P orthophosphate solutions using Fe(II)-to-orthophosphate equivalence ratios of 1.5 and 0.33, respectively (ferrous iron dosages of 48.6 mg/ℓ and 10.8 mg/ℓ). The ferrous iron dosage in Experiment 13 was the same as that in Experiment 12, but the orthophosphate concentration was reduced to 4.0 mg/ℓ P (Fe(II)-to-orthophosphate equivalence ratio = 1.0).

The experimental results for Experiment 11 are presented in Table 6. The solution pH decreased slightly in the first half hour and increased slightly in the second half hour. Visual observation of the test solution during this experiment indicated a substantial increase in solution turbidity during the second half of the first hour (i.e. concurrent with the slight rise in solution pH). As indicated in Table 6, the percent total orthophosphate removal during this 1/2 hour period increased from 86% to 99%. This additional removal of orthophosphate, however, was not accompanied by a proportionate rise in the extent of ferrous iron precipitation. No significant change in the concentration of either reactant was observed after the first hour. For a reaction time of 5 hr, maximum removals of orthophosphate and ferrous iron were 99 and 76%, respectively. The results thus indicate that at a pH close to 8, not all the excess ferrous iron added to the phosphate solution precipitates with the phosphate or as hydroxide. Turbidity measurements made on an aliquot removed at the end of the 5 hr test period yielded a value of 63 JTU. All precipitates retained on 100 mμ membrane filtrates were initially light green in color. On exposure to air, the precipitates from 15 min and 30 min samples turned yellow whereas the precipitates from 1 to 5 hr samples developed a dark bluish green color.

TABLE 6

ORTHOPHOSPHATE PRECIPITATION WITH Fe(II) AT AN Fe(II)-TO-ORTHOPHOSPHATE EQUIVALENCE RATIO OF 1.5[a]

(Experiment 11)

Time[b]	pH[c]	Percent Reactant Removal	
		P	Fe
0 min		0	0
5 min	7.88	-[d]	-
15 min	7.81	79.5	67.9
30 min	7.81	86.3	71.4
45 min	7.90	-	-
1 hr	7.95	99.0	75.1
1-1/4 hr	7.90	-	-
2 hr	7.78	99.0	76.2
3 hr	7.71	99.3	75.5
4 hr	7.68	99.4	76.4
5 hr	-	99.2	74.5

[a] Initial orthophosphate concentration = 12 mg/ℓ P

[b] Time from the start of Fe(II) addition and beginning of pH adjustment

[c] pH adjustment made initially by addition of 0.1 N NaOH concurrent with and for about 4 min after the addition of Fe(II)

[d] - indicates no measurements were made

Comparison of the results of Experiment 11 with those for Experiment 8 (Table 5) indicates that in terms of the patterns of change in pH, reactant removal and precipitate color, orthophosphate precipitation at an Fe(II)-to-orthophosphate equivalence ratio of 1.5 is very similar to that for a reactant ratio of 1.0.

The data on formation and characteristics of the precipitates and on changes in solution pH for Experiments 12 and 13 are presented in Table 7. (In these experiments no data were collected on the change in residual reactant concentration with time.) Comparison of the results of Experiment 12 with the results of Experiments 11 (Table 6), 8 (Table 5) and 4 (Table 4) indicates that for an initial orthophosphate concentration of 12 mg/ℓ P, the patterns of change in solution pH and turbidity and in the color of the precipitates are essentially unaffected by the change in Fe(II) concentration. In Experiment 13 there were essentially no changes in solution pH and no visible formation of turbidity during the first 2 hr of the test. After 2 hr and 20 min, however, precipitation occurred accompanied by a rapid drop in solution pH. Only the 3 to 5 hr precipitates in this experiment developed the characteristic bluish color of vivianite. Comparison of the results of Experiments 12 and 13 thus indicates that the rate of orthophosphate precipitation with Fe(II) is lower at lower orthophosphate concentrations.

Effect of Anions on Orthophosphate Precipitation with Fe(II). The effect of anions on orthophosphate precipitation with Fe(II) was evaluated in two experiments. Ferrous ammonium sulfate had been used as source of Fe(II) in Experiments 1-13. To compare the effect of sulfate ion with an anion such as perchlorate which has a lower tendency for complexing cations, an experiment was performed with ferrous perchlorate (orthophosphate 12 mg/ℓ P, reactant equivalence ratio 1.0, initial pH 7.98). The pattern of turbidity development and change in precipitate color in this experiment were similar to those in the experiments using ferrous ammonium sulfate.

Experiment 14 was an evaluation of the effect of bicarbonate ion (420 mg/ℓ $NaHCO_3$) on orthophosphate precipitation with Fe(II). The results are presented in Table 8. The solution pH in this experiment decreased slightly during the first hour and increased thereafter. The rise in solution pH is probably due to the expulsion of some CO_2 from the system due to purging with argon. (This was verified in one experiment in which a solution of 210 mg/ℓ $NaHCO_3$ was treated with argon in the same manner as the phosphate test solution; the pH rose from an initial value of 8.27 to 8.57 by the end of 5 hr.) The data in Table 8

TABLE 7

EFFECT OF ORTHOPHOSPHATE CONCENTRATION ON PHOSPHATE PRECIPITATION WITH Fe(II)

Time[a]	Experiment 12[b]		Experiment 13[c]	
	pH[d]	Precipitate Color After Exposure to Air	pH[d]	Precipitate Color After Exposure to Air
15 min	7.97	Yellow	7.93	Faint yellow
25 min	7.78	-[e] [f]	7.91	-
30 min	7.69	Blue-green	7.91	Faint yellow
1 hr	7.50	Blue	7.88	Faint yellow
2 hr	7.50	Blue	7.87	Faint yellow
2 hr and 20 min	7.45	-	7.87	- [f]
3 hr	7.45	Blue	7.42	Pale bluish-yellow
4 hr	7.45	Blue	7.29	-
5 hr	7.43	Blue	7.22	Pale bluish-yellow

[a] Time from the start of Fe(II) addition and beginning of pH adjustment

[b] Fe(II) = 10.8 mg/ℓ; P = 12 mg/ℓ; Fe(II)-to-orthophosphate equivalence ratio = 0.33

[c] Fe(II) = 10.8 mg/ℓ; P = 4 mg/ℓ; Fe(II)-to-orthophosphate equivalence ratio = 1.0

[d] pH adjustment made initially by addition of 0.1 N NaOH concurrent with and for close to 4 min after the addition of Fe(II)

[e] - indicates that sample was not collected

[f] Substantial increase in turbidity was observed

TABLE 8

EFFECT OF BICARBONATE ALKALINITY ON THE PRECIPITATION OF ORTHOPHOSPHATE WITH Fe(II)[a]

(Experiment 14)

Time[b]	pH[c]	Percent Reactant Removal	
		P	Fe
0 min		0	0
5 min	7.88	56.1	75.0
15 min	7.88	59.8	81.5
30 min	7.85	62.4	88.9
1 hr	7.90	79.0	90.4
2 hr	8.10	86.8	96.3
4 hr	8.18	-[d]	-
5 hr	8.28	90.3	98.4

[a] Initial orthophosphate concentration 12 mg/ℓ P, initial bicarbonate alkalinity = 420 mg/ℓ $NaHCO_3$, Fe(II)-to-orthophosphate equivalence ratio = 1

[b] Time from start of Fe(II) addition

[c] No supplementary pH adjustment made with NaOH; initial pH after addition of Fe(II) (time ≈ 20 sec) = 7.88

[d] - indicates no measurements made

indicate that a substantial portion of orthophosphate was precipitated in the first 5 min. In this experiment, as with the experiments with pure orthophosphate solutions, there was a significant increase in orthophosphate removal in the second half of the first hour; that orthophosphate and ferrous iron removals were essentially complete in about 2 hr. For the reaction time of 5 hr, maximum orthophosphate and ferrous iron removals were 90 and 98%, respectively. The corresponding data for Experiment 8 (Table 5) conducted in the absence of bicarbonate alkalinity were 94% P, 97% Fe. Considering the small difference between the solution pH in the two experiments and allowing for a certain degree of experimental error, the results would thus indicate that for the conditions tested the removal efficiencies are not appreciably affected by the presence of bicarbonate ion.

Orthophosphate Precipitation with Fe(II) from Actual Wastewater (Experiment 15). The data obtained in the phosphate precipitation from secondary effluent (Wastewater #1, Table 1) are presented in Table 9. The addition of Fe(II) to the wastewater resulted in a small immediate (within about 20 sec) drop in pH followed by a subsequent gradual further decrease which lasted for about 1 hr. After 1 hr, the solution pH gradually increased, probably due to the expulsion of some CO_2 from the system due to purging with argon. As indicated by the data in Table 9, a substantial portion of the orthophosphate was precipitated in the first 15 min and the increase in the percent reactant removal was small after the second hour. For the reaction time of 5 hr, maximum removals of orthophosphate and iron were 98 and 66%, respectively. The removal efficiencies indicate a near 1:1 Fe(II)-orthophosphate reaction stoichiometry. As with the experiment with pure orthophosphate solution (Experiment 11), not all the excess ferrous iron added to the sample precipitated with the orthophosphate or as hydroxide.

Visual observation of the wastewater sample during the precipitation experiment indicated that little turbidity was formed during the first 15 min after the addition of Fe(II). A substantial amount of turbidity, however, was formed after 15 min. All precipitates retained on 100 mμ membrane filters were initially light green in color. On exposure to air, the precipitate from the 15 min sample remained light green. The 30 min sample developed a darker green color. All 1 to 5 hr samples developed a blue-green color. As was discussed earlier, the pattern of color change from light green to blue is reported to be a characteristic of vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$.

TABLE 9

ORTHOPHOSPHATE PRECIPITATION FROM SECONDARY EFFLUENT WITH Fe(II) IN THE ABSENCE OF DISSOLVED OXYGEN[a]

(Experiment 15)

Time[b]	pH[c]	Percent Reactant Removal	
		P	Fe
0 min	7.80	0	0
5 min	7.30	-[d]	-
15 min	7.21	48.2	33.5
30 min	7.02	71.9	47.3
1 hr	7.03	85.3	54.3
2 hr	7.25	94.1	59.1
3 hr	7.42	95.2	61.7
4 hr	-	95.8	60.9
5 hr	7.77	98.0	65.9

[a]Wastewater #1 (Table 1); Fe(II)-to-orthophosphate equivalence ratio = 1.5

[b]Time after start of Fe(II) addition; Fe(II) added after the sample had been purged with argon for about 1 hr

[c]No supplementary pH adjustment made with NaOH; initial pH after addition of Fe(II) (time ≃ 20 sec) = 7.40

[d]- indicates no measurements made

In terms of the rate of orthophosphate removal, the general pattern of turbidity development and the change in precipitate color on exposure to air, the precipitation of orthophosphate with Fe(II) from actual wastewater appears to be very similar to that for orthophosphate precipitation from pure orthophosphate solutions and from orthophosphate solutions containing $NaHCO_3$.

Precipitation of Pyro- and Tripolyphosphates with Fe(II) (Experiments 16 and 17). Solutions containing orthophosphate were used in Experiments 1 through 14. In some wastewaters, however, condensed phosphates such as pyro- and tripolyphosphates account for a significant portion of the total phosphate content. The effectiveness of ferrous iron for the precipitation of condensed phosphates was examined in two experiments (Experiments 16 and 17), conducted on 1.16 meq/ℓ solutions of pyrophosphate (18 mg/ℓ P) and tripolyphosphate (21.6 mg/ℓ P) using an equivalent reactant ratio of 1.0. The results are presented in Table 10.

In the pyrophosphate experiment, the solution pH decreased slightly at first reaching a minimum value of 7.81 by the end of 45 min. After 45 min, the pH increased slightly reaching a maximum value of 7.98 by the end of the first hour and decreased gradually thereafter. A substantial amount of turbidity was formed during the last quarter of the first hour. In the tripolyphosphate experiment, there was a small decrease in pH, but the solution remained clear during the 5 hr observation period.

In both Experiments 16 and 17, the precipitates retained on 100 mμ membrane filters were initially light green. On exposure to air, all precipitates in the tripolyphosphate test and the 15 min precipitate in the pyrophosphate test turned yellow and all 1 to 5 hr precipitates in the pyrophosphate test developed a yellow-green color. As indicated in Table 10, maximum phosphate and iron removals obtained during the 5 hr test period were 87% P and 91% Fe in Experiment 17. The data for orthophosphate precipitation at 12 mg/ℓ P level (also 1.16 meq/ℓ) for Experiment 8 (Table 5), indicate maximum orthophosphate and iron removals of 94% and 97%, respectively. Thus, on an equivalent basis and at the pH levels examined, orthophosphate is more efficiently precipitated than pyrophosphate which in turn is more efficiently precipitated than tripolyphosphate. The data on the patterns of change in pH and on precipitate formation indicate a more rapid rate of precipitation for orthophosphate than for pyrophosphate.

TABLE 10

PRECIPITATION OF PYRO- AND TRIPOLYPHOSPHATE WITH Fe(II) IN THE ABSENCE OF DISSOLVED OXYGEN[a]

Time[b]	Experiment 16 Pyrophosphate			Experiment 17 Tripolyphosphate		
	pH[c]	Percent Reactant Removal		pH[c]	Percent Reactant Removal	
		P	Fe		P	Fe
0 min		0	0		0	0
5 min	7.94	-[d]	-	7.91	-	-
15 min	7.89	20.7	27.3	7.89	10.4	10.3
30 min	7.85	-	-	7.87	10.6	11.6
45 min	7.81	-	-	7.85	-	-
1 hr	7.98	76.7	79.2	7.83	10.1	9.6
2 hr	7.96	85.7	89.3	7.80	-	-
3 hr	-	86.6	90.5	7.77	9.5	9.0
4 hr	-	86.4	91.5	7.72	-	-
5 hr	7.59	84.5	88.3	7.71	-	-

[a]Phosphate initially present at 1.16 meq/ℓ; 18 mg/ℓ P pyrophosphate and 21.6 mg/ℓ P tripolyphosphate; Fe(II)-to-phosphate equivalence ratio = 1.0

[b]Time from start of Fe(II) addition

[c]pH adjustment made initially be addition of 0.1 N NaOH; pH at the temination of pH adjustment (time ~ 4 min) = 8.00, and 7.98 in the experiments with pyro- and tripolyphosphate, respectively

[d]- indicates no measurements made

Comparison of Phosphate Precipitation Using Fe(II) with Phosphate Precipitation Using Fe(III) and Al(III) Salts

Effect of pH on Orthophosphate Precipitation. The precipitation of orthophosphate with Fe(III) and Al(III) was recently investigated in some detail.[4] Figure 5 compares the orthophosphate precipitation results for Fe(II), Fe(III) and Al(III) salts at an equivalence reactant ratio of 1.0. From the data in this figure it may be seen that the pH of maximum orthophosphate removal is in the vicinity of 8 for Fe(II), close to 3.5 for Fe(III) and about 5 for Al(III). Also, for the conditions tested, minimum residual orthophosphate concentrations of 0.7, 1.8 and 3.5 mg/ℓ P were obtained with Fe(II), Fe(III), and Al(III), respectively. Thus, at the respective pH of maximum effectiveness and on an equivalent basis, ferrous iron is more effective than either Al(III) or Fe(III) for the precipitation of orthophosphate. The data in Figure 5 indicate that, compared to Fe(III) and Al(III), the effectiveness of Fe(II) for phosphate precipitation extends over a relatively narrow pH range. It should, however, be noted that the results for experiments with Fe(II) are for a reaction time of 5 hr. While in the vicinity of pH 8 and at higher pH levels, Fe(II)-orthophosphate reactions may be essentially complete in 5 hr, at lower pH levels, a longer time may be necessary to achieve equilibrium and attain maximum removal of phosphates.

The pH of most wastewaters is in the 7 to 8 range. To reach the optimum precipitation pH with Fe(III) and Al(III), a substantial amount of acid or a considerable excess of coagulant must be added to the wastewater to overcome its natural buffer capacity. When Fe(II) is used for phosphate precipitation in the absence of dissolved oxygen, such an extensive pH adjustment would not be necessary. Any minor pH adjustments can be accomplished by addition of a small quantity of lime. In the present study no data were collected on the effect of pH on orthophosphate precipitation with Fe(II) from actual wastewater. In water and wastewater treatment with Al(III) and Fe(III) salts, the treatment efficiency-pH curve has been shown to be affected by the presence of diverse ions. It is possible that the phosphate precipitation-pH curve for wastewater is somewhat different (perhaps broader) than that shown in Figure 5 for a pure phosphate solution.

The reaction of orthophosphate with both Al(III) and Fe(III) salts has been shown to be very rapid and completed in less than 1 sec.[4] At and near the pH of maximum orthophosphate removals, readily settleable flocs are formed with both cations and any excess Al(III) and Fe(III) added to the phosphate solution precipitates with the phosphate or as hydroxide.[4] The reaction of ferrous iron with orthophosphate

in the absence of dissolved oxygen, however, is relatively slow and results in the formation of a fine and poorly settleable precipitate. Also, with ferrous iron not all the excess cation added to the phosphate solution precipitates with the phosphate or as hydroxide.

Application of Solubility Data to the Analysis of Phosphate Precipitation Results. The pH dependence of orthophosphate removal efficiency with hydrolyzing cations can be explained in terms of the solubility of the precipitates formed and the competition between hydroxide and orthophosphate ions to react with the cation. As was pointed out before, orthophosphate precipitation with Fe(II) results in the formation of ferrous phosphate. Table 11 contains some of the equilibrium relationships pertinent to the solubility of ferrous phosphate in water. Except for a value of 1.3×10^{-30} recently reported by Singer,[9] no data have been reported on the solubility constant of ferrous phosphate. The data compiled by Sillen and Martell[10] indicate that the values reported for the equilibrium constant for reaction 4 (Table 11) varies over several orders of magnitude. However, since the majority of the values listed are close to 10^7, this value was selected as a representative value for use in the present analysis. On the basis of the data in Table 11 and the assumptions that (a) $Fe(OH)_2$ and $Fe_3(PO_4)_2$ are the only solid phases formed, and (b) the formation of soluble Fe(II)-phosphate complexes can be neglected, a mathematical expression can be derived for the equilibrium total soluble orthophosphate concentration as a function of pH.

Equilibria 1-3 (Table 11) define the fraction α of the total orthophosphate ion (P_T) which exists in solutions as PO_4^{-3} ions at any pH level.

$$\alpha = \frac{[PO_4^{-3}]}{[P_T]} = \frac{K_1K_2K_3}{K_1K_2K_3 + K_1K_2[H^+] + K_1[H^+]^2 + [H^+]^3} \qquad (a)$$

where brackets represent concentrations in moles/ℓ and K_1, K_2 and K_3 are the equilibrium constants for reactions 1, 2 and 3, respectively. From equilibria 4, 5 and 6, a similar expression can be obtained for the fraction β of the soluble Fe(II) species which exists as Fe^{+2} ion.

$$\beta = \frac{[Fe^{+2}]}{[Fe(II)_T]} = \frac{[H^+]^3}{[H^+]^3 + K_4K_w[H^+]^2 + K_5K_6K_w^3} \qquad (b)$$

TABLE 11

EQUILIBRIUM RELATIONSHIPS FOR ORTHOPHOSPHATE-Fe(II) SYSTEM

No.	Equilibrium	Equilibrium Constant (25°C)	Reference
	I. Ionization of orthophosphate		
1	$H_3PO_4 = H_2PO_4^- + H^+$	7.11×10^{-3}	11
2	$H_2PO_4^- = HPO_4^{-2} + H^+$	7.99×10^{-8}	11
3	$HPO_4^{-2} = PO_4^{-3} + H^+$	4.8×10^{-13}	11
	II. Cation Hydrolysis		
4	$Fe^{+2} + OH^- = Fe(OH)^+$	10^7	10
5	$Fe^{+2} + 2\ OH^- = Fe(OH)_2(s)$	1.25×10^{15}	12
6	$Fe(OH)_2(s) + OH^- = Fe(OH)_3^-$	8.3×10^{-6}	13
	III. Phosphate Solubility		
7	$Fe_3(PO_4)_2 = 3Fe^{+2} + 2PO_4^{-3}$	1.3×10^{-30}	9

where K_4, K_5 and K_6 are equilibrium constants for reactions 4, 5 and 6 (Table 11), respectively, and K_w is the ionization constant for water. From equilibrium 7

$$\left[Fe^{+2}\right]^3 \left[PO_4^{-3}\right]^2 = K_7 \tag{c}$$

or

$$\left\{\beta\left[Fe(II)_T\right]\right\}^3 \left\{\alpha\left[P_T\right]\right\}^2 = K_7 \tag{d}$$

When $Fe_2(PO_4)_3$ is the only source of orthophosphate and ferrous iron in water, dissolution of one mole of ferrous phosphate would result in the release of 3 moles of $Fe(II)_T$ and 2 moles of P_T, i.e.,

$$1.5\left[P_T\right] = \left[Fe(II)_T\right] \tag{e}$$

Substituting equation (e) in equation (d):

$$\left\{\beta\,(1.5)\left[P_T\right]\right\}^3 \left\{\alpha\left[P_T\right]\right\}^2 = K_7 \tag{f}$$

or

$$\left[P_T\right] = 8.26 \times 10^{-7}\ \beta^{-0.6}\ \alpha^{-0.4} \tag{g}$$

When values of α and β from equations (a) and (b) are substituted in equation (g), a relationship is obtained which expresses the concentration of total soluble orthophosphate which is in equilibrium with the solid phase at various pH levels.

$$\left[P_T\right] = (8.26 \times 10^{-7}) \left\{\frac{[H^+]^3}{[H^+]^3 + K_4K_w[H^+]^2 + K_5K_6K_w^3}\right\}^{-0.6} \left\{\frac{K_1K_2K_3}{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3}\right\}^{-0.4} \tag{h}$$

Curve A in Figure 6 is a plot of equation (h) based on the values listed in Table 11 for the various constants. This curve indicates a pattern of pH dependency similar to that observed in the orthophosphate precipitation experiments with Fe(II) (curve C). In contrast to the experimental results, however, equation (h) predicts a higher level of residual orthophosphate. Four possible explanations may be offered for this discrepancy. First, the actual solubility constant for ferrous phosphate may be lower than value of 1.3×10^{-30} used in the computation of Curve A. Second, in the phosphate precipitation experiments some of the soluble phosphate is removed by adsorption on the precipitating ferrous phosphate or hydroxide. Third, equilibria other than those listed in Table 11 may also be involved in the precipitation system. Fourth, the actual equilibrium constants for Fe(II) hydrolysis reactions (reactions 4-6, Table 11) may be lower than those listed in Table 11. In the calculation of Curve A (Figure 6), a value of $K = 10^7$ had been assumed for the first hydrolysis reaction of Fe(II) (reaction 4, Table 11). Curve B (Figure 6) is based on the data in Table 11, but using a value of 5×10^5 (reported by Leussing and Kolthoff[12]) for reaction 4. As indicated in Figure 6, Curve C indicates lower levels of residual orthophosphate and the values in the vicinity of the pH of minimum solubility are in fair agreement with the experimental results. Although neither Curve A nor Curve B coincides with the experimental results (perhaps largely due to the uncertainty regarding the true values of the various equilibrium constants), in terms of the general effect of pH on the solubility of ferrous phosphate, the experimental results are in reasonable accord with theoretical consideration.

Orthophosphate precipitations with Fe(III) and Al(III) are not amenable to simple mathematical treatment due to the complex and poorly understood chemistries of the hydrolysis reactions of Al(III) and Fe(III) and the uncertainty regarding the exact chemical nature of the precipitates formed at different pH levels. Although $AlPO_4$ and $FePO_4$ have been suggested as the insoluble reaction products, the formation of precipitates of such composition is not consistent with the observed reaction stoichiometry which indicates that even under optimum pH conditions hydrolysis products of Al(III) and Fe(III) and not the simple Fe^{+3} and Al^{+3} ions are involved in orthophosphate precipitation[4] (i.e., the precipitates formed are hydroxy cation phosphates and not $AlPO_4$ or $FePO_4$). Despite these complexities, considerations similar to those presented above for the Fe(II)-orthophosphate system may be used to explain the pH-dependency of orthophosphate removal with both Fe(III) and Al(III). Thus with these cations, as with Fe(II), the optimum orthophosphate removal pH and the extent of orthophosphate removal

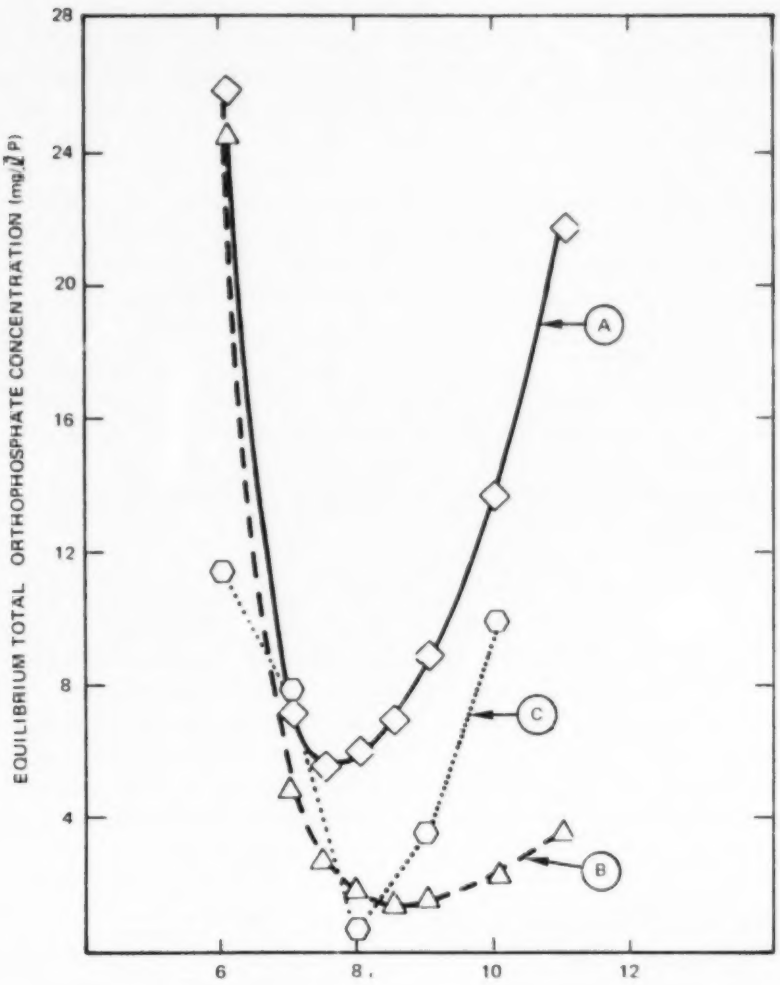


FIGURE 6. SOLUBILITY DIAGRAM FOR FERROUS PHOSPHATE

CURVES A & B ARE CALCULATED DATA BASED ON EQUILIBRIUM DATA SHOWN IN TABLE II.
CURVE A IS FOR $K_4 = 1 \times 10^7$; CURVE B IS FOR $K_4 = 5 \times 10^5$
CURVE C PRESENTS THE RESULTS OF ACTUAL PRECIPITATION TESTS FROM FIGURE 5.

at various pH levels are determined by the solubility product constants for the insoluble reaction products and by the equilibrium constants for orthophosphate ionization reactions and cation hydrolysis. Solubility product values of 1.25×10^{-15}, 10^{-36}, and 10^{-32} which have been reported for $Fe(OH)_2$, $Fe(OH)_3$ and $Al(OH)_3$, respectively,[12, 14] indicate that ferrous hydroxide precipitates at a higher pH than ferric and aluminum hydroxides. For a 10^{-3} M cation concentration, for example, the pH at which cation hydroxide precipitation commences are 8.0, 2.0 and 3.3 for Fe(II), Fe(III) and Al(III), respectively. The observed higher pH of orthophosphate precipitation with Fe(II) can be explained in terms of a combination of two factors, namely, that Fe(II) hydrolyzes at a higher pH than Al(III) and Fe(III) and that the phosphate precipitates formed with Fe(III) and Al(III) have lower solubilities than ferrous phosphate.

Al(III) and Fe(III) hydrolyze in solution to a considerable extent. Accordingly, even under optimum pH conditions, their potential capacity for phosphate removal is not fully realized. Based on the data in Figure 5, the maximum orthophosphate removal capacity for Fe(III) and Al(III) are 0.85 and 0.71 moles per mole of cation precipitated, respectively. Compared to Al(III) and Fe(III), Fe(II) has a considerably lower tendency to hydrolyze and on an equivalent basis is more effective in precipitating orthophosphates (see Figure 5).

Orthophosphate Precipitation with Fe(II) in the Presence of Dissolved Oxygen

Wastewater treatment with ferrous iron under conditions where dissolved oxygen is totally excluded from the system is not practical from the standpoint of large scale application. In the presence of even a small amount of dissolved oxygen, oxidation of some of the ferrous iron to ferric iron is inevitable. To simulate actual conditions in wastewater treatment, a number of experiments were conducted in which no precautions were taken to exclude dissolved oxygen from the system. A discussion of the results of the experiments will follow.

Effect of Dissolved Oxygen on the Rate and Efficiency of Orthophosphate Removal (Experiments 18-20). Table 12 presents the results of an orthophosphate precipitation test (Experiment 18) with ferrous iron in the presence of dissolved oxygen. Comparison of the results of this experiment with the results of Experiment 14 (Table 8) conducted in the absence of dissolved oxygen indicates that the presence of dissolved oxygen results in a drop in pH, rapid removal of orthophosphate and near quantitative precipitation of iron. Comparison of the maximum orthophosphate removal efficiencies in the two

TABLE 12

ORTHOPHOSPHATE PRECIPITATION WITH Fe(II) IN THE PRESENCE OF DISSOLVED OXYGEN[a]

(Experiment 18)

Time[b]	pH[c]	Percent Reactant Removal	
		P	Fe
0 min		0	0
5 min	7.23	71.8	≃100
15 min	7.30	71.8	≃100
30 min	7.32	71.8	-
1 hr	7.50	71.4	-
2 hr	7.78	71.4	≃100
3 hr	7.95	-[d]	-
4 hr	8.08	-	-
5 hr	8.18	69.9	-

[a] Initial orthophosphate concentration 12 mg/ℓ P; initial bicarbonate alkalinity 420 mg/ℓ $NaHCO_3$; Fe(II)-to-orthophosphate equivalence ratio = 1.0

[b] Time from start of Fe(II) addition

[c] No supplementary pH adjustment made with NaOH; initial pH after addition of Fe(II) (time ≃ 20 sec) = 7.23

[d] - indicates no measurements made

experiments (72% vs 90%) also indicates that under the conditions tested the efficiency of orthophosphate removal with Fe(II) is reduced in the presence of dissolved oxygen. (It should be noted, however, that for reaction times less than about 1 hr, the phosphate removal efficiency is higher in the presence than in the absence of dissolved oxygen.)

Table 13 contains data for two experiments (Experiments 19 and 20) conducted on a secondary effluent (wastewater #2, Table 1) using Fe(II)-to-orthophosphate equivalence ratios of 0.5 and 1.5. In both experiments the solution pH decreased gradually in the first hour and then increased slightly during the second hour. Comparison of the data for Experiments 19 and 20 with those for Experiment 18 (Table 12) indicates that while the initial pH of the reacted mixtures was not significantly different in the three experiments, the reactant removal was slower in the experiment with the wastewater. It is interesting to note that in Experiment 20 nearly all the excess ferrous iron added to the wastewater precipitated after 2 hr and this is in contrast to the results of Experiment 15 (Table 9, conducted in the absence of dissolved oxygen) which indicates an incomplete precipitation of the excess iron.

Some Fundamental Considerations Regarding Oxidation of Ferrous Iron by Dissolved Oxygen and Its Effect on Phosphate Precipitation. Dissolved oxygen in water oxidizes ferrous iron to ferric iron. The rate of oxidation of ferrous iron by oxygen in a bicarbonate buffer system has been shown to follow the expression

$$\frac{-d\,[Fe(II)]}{dt} = k\,[Fe(II)]\,[OH^-]^2\,[O_2]$$

where brackets denote concentrations in mole/ℓ.[15] The value of k at 20.5°C in the bicarbonate buffer system is about 1×10^{16} liter^3 mole^{-3} min^{-1}.[15] From this equation it may be seen that the rate of oxidation of ferrous iron is strongly dependent on solution pH and also on Fe(II) and dissolved oxygen concentrations. Thus in the presence of 0.5 mg/ℓ dissolved oxygen, the half-life of ferrous iron would be 7.5 hr at pH = 7.0 and 4.5 min at pH 8.0. The corresponding half-life values for a dissolved oxygen concentration of 5 mg/ℓ would be 45 min and 0.5 min, respectively. The rate of oxidation of ferrous iron by dissolved oxygen has also been found to be affected by the presence of diverse ions. For example, substantial increases in the oxidation rate have been observed in the presence of orthophosphate, pyrophosphate and a number of other anions.[15] In the aeration treatment of ground waters containing ferrous iron, the presence of dissolved organics has been found to lower the efficiency of iron removal.[16] No data are available on the rate of oxidation of ferrous iron in the wastewater

TABLE 13

ORTHOPHOSPHATE PRECIPITATION WITH Fe(II) FROM SECONDARY EFFLUENT IN THE PRESENCE OF DISSOLVED OXYGEN[a]

Time[b]	Experiment 19[c]			Experiment 20[d]		
	pH[e]	Percent Reactant Removal[f]		pH[e]	Percent Reactant Removal[f]	
		P	Total Fe		P	Total Fe
0 min	7.60	-[g]	-	7.60	-	-
1 min	7.48	-	-	7.41	-	-
5 min	7.40	-	-	7.15	-	-
10 min	7.35	-	-	7.10	-	-
15 min	7.31	53	94	7.09	96	78
30 min	7.30	-	-	7.08	-	-
1 hr	7.30	-	-	7.06	-	-
1-1/2 hr	7.35	-	-	7.10	-	-
2 hr[h]	7.35	58	~100	7.10	~100	~100

[a] Wastewater #2, Table 1

[b] Time after Fe(II) addition

[c] Fe(II)-to-orthophosphate equivalence ratio = 0.5

[d] Fe(II)-to-orthophosphate equivalence ratio = 1.5

[e] No supplementary pH adjustment made with NaOH

[f] Because of the very fine nature of the precipitates formed, it took about 30 min for each aliquot to filter

[g] - indicates no measurements made

[h] The turbidity of the reacted mixture at the end of 2 hr was 35 JTU in Experiment 19 and 60 JTU in Experiment 20

environment. In wastewater treatment with ferrous iron in the presence of dissolved oxygen, the phosphate precipitation system becomes complicated by the generation and subsequent hydrolysis of Fe(III) and in this regard the system differs from phosphate precipitation with pure Fe(III) and with Fe(II) in the absence of dissolved oxygen.

In the absence of cation hydrolysis reactions, oxidation of ferrous iron to ferric iron should result in an increase in the efficiency of phosphate removal, since on a molar basis the capacity of ferric iron for phosphate removal should be 50% higher than that of ferrous iron. However, because ferric iron hydrolyzes in solution to a greater extent than ferrous iron, oxidation of ferrous iron may or may not result in an increase in orthophosphate removal efficiency. If no oxidation of ferrous iron had occurred in Experiment 19, a maximum orthophosphate removal efficiency of only 50% would have been expected. The observed orthophosphate removal in this experiment, however, was higher (58%) thus suggesting a partial or total oxidation of ferrous iron. In the absence of hydrolysis reactions, a phosphate removal efficiency of 75% would have been expected from the quantitative oxidation of ferrous iron. The observed phosphate removal efficiency, however, is lower than this theoretical amount (58 vs 75%), thus suggesting either partial oxidation of ferrous iron with or without subsequent hydrolysis of ferric iron, or total oxidation of ferrous iron with subsequent hydrolysis of ferric iron. Even if total oxidation of ferrous iron is assumed, a phosphate removal efficiency of 58% is higher than what can be obtained at a pH of close to 7.35 with an Fe(III)-to-phosphate molar ratio of 0.75 when ferric iron from a stock solution is used for phosphate precipitation. (According to the data in Figure 5, the phosphate removal efficiency is 63% at pH 7.35 for an Fe(III)-to-orthophosphate molar ratio of 1.0.) The observed increased efficiency may be attributed to the in situ generation of ferric iron which, according to Singer and Stumm,[17] promotes a more effective contact between the iron and the phosphate.

Singer and Stumm[17] studied and compared the precipitation of orthophosphate (at a 10^{-4} M level) from a bicarbonate solution by direct addition of Fe(III) and by homogeneous generation of Fe(III) through in situ oxidation of previously added Fe(II). The experiments were conducted at pH values of 4.5, 5.0, 5.5, 6.0, 6.5, and 7.0 using iron concentrations ranging from 10^{-5} to 10^{-3} M. At lower pH levels ozone was continuously bubbled through the solution to assure quantitative oxidation of ferrous iron. With the exception of the results at pH 7.0, the degree of removal was generally enhanced by the utilization of the homogeneous precipitation technique. The results of the experiments at pH 7.0, however, are questionable since a possibility exists

that the precipitates formed at this pH with homogeneously generated Fe(III) were too fine to be quantitatively retained by the 1.2 μ membrane filters employed for sample filtration. When Fe(III) is generated homogeneously within the solution, it is uniformly distributed throughout the system thereby promoting a direct contact between the iron and the phosphate. On the other hand, when ferric iron is added from an external source, due to the formation of "short-lived" regions of high Fe(III) concentration, some of the Fe(III) may be coprecipitated through hydrolysis. The precipitation of phosphates from wastewater by homogeneously generated ferric iron has not been investigated in detail and the parameters which influence process efficiency are not defined.

Formation and Settling Characteristics of the Precipitates in Wastewater Treatment with Fe(II) in the Presence of Dissolved Oxygen (Experiments 21-26). In any application of the chemical precipitation to the treatment of wastewater for phosphate removal, the properties of the precipitates formed are of major engineering concern. Table 14 presents data on the effect of Fe(II) dosage on the settleability of the precipitates formed in the treatment of secondary effluent with Fe(II) in the presence of dissolved oxygen. Although the actual concentration of dissolved oxygen in these experiments was not determined, with the type of sample pretreatment and mixing employed, it would be reasonable to assume that the test solutions in all cases were nearly saturated with dissolved oxygen (~8 mg/ℓ dissolved oxygen). Immediately upon addition of Fe(II), all samples developed a milky-yellow color. By the end of 2 min of rapid mixing, floc formation was noted in all samples and the samples were all yellow in color. By the end of 30 min of settling, a significant amount of a yellowish precipitate had settled to the bottom in each jar. After 1-1/4 hr of settling, the solution in Experiment 21 was yellowish gray and the solutions in Experiments 22-26 were reddish-brown, with the intensity of the color increasing with the increase in Fe(II) dosage.

The turbidity data presented in Table 14 indicate that under the conditions of the experiments (a) the higher the Fe(II) dosage, the greater is the amount of turbidity formed, (b) with the exception of the sample with an Fe(II)-to-orthophosphate equivalence ratio of 0.4, there was an increase in turbidity after 15 min, thus suggesting the formation of additional precipitate, and (c) the precipitates formed with Fe(II) do not settle well and, even after standing overnight, all samples contained substantial amounts of turbidity.

At the end of 2 hr of settling, a portion of the wastewater from each experiment was filtered through Whatman #42 filter paper. The filtrates from Experiments 21 and 22 appeared colorless, whereas those from

TABLE 14

FORMATION AND SETTLING CHARACTERISTICS OF PRECIPITATES IN ORTHOPHOSPHATE PRECIPITATION FROM SECONDARY EFFLUENT WITH Fe(II) IN THE PRESENCE OF DISSOLVED OXYGEN[a]

Exp. No.	$Fe(II)/PO_4^{-3}$ Equivalence Ratio	pH[b]	Turbidity of Samples After Indicated Periods of Settling[c] (JTU)					
			2 min	5 min	15 min	1 hr	2 hr	≈20 hr
21	0.4	7.30	120	105	70	65	62	23
22	0.8	7.08	175	117	120	125	130	77
23	1.0	6.85	190	132	127	150	165	92
24	1.2	6.76	175	130	135	170	187	87
25	1.5	6.68	190	135	-	-	220	125
26	2.0	6.60	-[d]	-	150	200	-	127

[a] Wastewater #2, Table 1

[b] pH measured after 2 hr of settling

[c] Turbidity analysis made on sample aliquots removed from about 2.5 in. below the water surface

[d] - indicates no measurements were made

samples 23-26 were reddish-brown. On standing overnight, all filtrates developed turbidity which could be only partially removed by filtration through Whatman #42 paper. The amount of turbidity was especially significant in samples 24-26. These filtrates were refiltered through Whatman #42 filter papers. A portion of each new filtrate was subsequently filtered through a 100 mμ membrane filter. The new Whatman #42 filtrates and the 100 mμ membrane filtrates were analyzed for turbidity, phosphate and total iron content. The results are presented in Table 15.

The data in Table 15 indicate that some of the precipitates formed in the treatment of secondary effluent with Fe(II) are very fine and cannot be totally removed even by very fine filter papers (compare, for example, the turbidity data for 100 mμ and Whatman #42 filtrates in Table 15). Also, at the pH levels tested and for the Fe(II) concentrations used, iron precipitation appears to be slow and incomplete (especially at low pH and high Fe(II) concentration). In the present study, no data were collected on the effect of pH and level of dissolved oxygen on the rate of formation and settling properties of the precipitates. Since the rate of oxidation and hence precipitation of ferrous iron would depend on both pH and dissolved oxygen concentration, addition of a base and/or extended aeration of the wastewater would be necessary for the removal of excess ferrous iron. Thus, in secondary treatment plants employing the activated sludge process, best results should be obtained when ferrous iron is added to the wastewater ahead of the primary or activated sludge tanks. Aeration of the wastewater in the activated sludge tank should result in effective oxidation of ferrous iron. Also, the activated sludge flocs should aid in the agglomeration and subsequent removal of the phosphate precipitates by settling. When only primary treatment is employed, the addition of a base would be necessary for the precipitation of excess ferrous iron. These conclusions are consistent with the results obtained at Mentor, Ohio, and at Texas City, Texas, wastewater treatment plants where acid pickling wastes containing 6 to 9% iron (mainly ferrous but probably also containing some ferric iron) were used for the treatment of raw sewage.[2]

In the Texas City operation where an iron dosage of 19 mg/ℓ was used for the treatment of wastewater containing 5.8 mg/ℓ P phosphate (an iron-to-phosphate molar ratio of 1.75), the phosphate removal with iron in primary treatment was less than 1%. The bulk of the phosphate was removed in the aerator and final settler, yielding an overall phosphate removal of 81% with an effluent phosphate concentration of 1.1 mg/ℓ P. Although it was not reported, the low phosphate removal efficiency in primary treatment may have been due to

TABLE 15

ORTHOPHOSPHATE PRECIPITATION FROM SECONDARY EFFLUENT WITH Fe(II) IN THE PRESENCE OF DISSOLVED OXYGEN - ANALYSIS OF THE FILTRATES[a]

Exp. No.	$Fe(II)/PO_4^{-3}$ Equivalence Ratio	Analysis of Second Whatman #42 Filtrates[b]			Analysis of 100 mμ Membrane Filtrates[c]		
		Turbidity (JTU)	Orthophosphate (mg/ℓ P)	Total Iron (mg/ℓ Fe)	Turbidity (JTU)	Orthophosphate (mg/ℓ P)	Total Iron (mg/ℓ Fe)
21	0.4	0.6	7.25	<0.15	0.7	6.87	< 0.15
22	0.8	4.6	2.02	0.33	0.2	1.69	< 0.15
23	1.0	5.5	1.31	0.42	0.3	1.08	< 0.15
24	1.2	7.6	2.10	0.46	0.3	2.04	< 0.15
25	1.5	4.1	1.48	0.38	0.6	1.57	< 0.15
26	2.0	3.7	0.79	3.14	1.2	0.89	0.83

[a] Wastewater #2, Table 1

[b] At the end of 2 hr settling (see Table 14); samples were filtered through Whatman #42 filter papers. On standing overnight, all filtrates developed turbidity. These filtrates were filtered through Whatman #42 filter paper and the new filtrates analyzed for turbidity, orthophosphate and total iron content

[c] The second Whatman #42 filtrates were filtered through 100 mμ membrane filters and analyzed for turbidity, orthophosphate and total iron content

any, a combination, or all of the following factors: (a) formation of fine and non-settleable precipitates, (b) inadequate reaction time, and (c) formation of soluble organic-iron complexes. At Mentor, Ohio, for an average influent phosphate concentration of 15.7 mg/ℓ P a phosphate removal efficiency of 46% was obtained in the primary treatment with an iron dosage of 50 mg/ℓ (an iron-to-phosphate molar ratio of 1.71). When lime (55 mg/ℓ) was used in conjunction with iron (43 mg/ℓ), the phosphate removal efficiency was increased to 76%. The primary removal efficiency was raised to 83.5% by using 0.4 mg/ℓ of anionic polymer in conjunction with 40 mg/ℓ of iron and 66 mg/ℓ of lime. The function of base (lime or sodium hydroxide) in improving the removal efficiency is not clearly understood, although it is asserted to be one of floc conditioning and not that of pH effect per se.[18] It is possible that the improvement in flocculation is a result of a change in particle surface charge, presumably brought about by the addition of base. The effect of pH on particle charge and the role of particle charge in the agglomeration of the flocs have not been investigated for phosphate removal by addition of Fe(II).

Settling Properties of the Precipitates Formed in Phosphate Precipitation Using Al(III) and Fe(III)

To compare the settling properties of the precipitates formed in the treatment of secondary effluent with Fe(II) with those of the precipitates formed with Fe(III) and Al(III) salts, experiments were conducted to evaluate the settling rates for the Fe(III)- and Al(III)-orthophosphate systems. The results are presented in Tables 16 and 17.

Comparison of the turbidity data presented in Tables 16 and 17 with the turbidity data for the experiments using Fe(II) (Table 14), indicates several interesting points. First, in all experiments with Al(III) and Fe(III) the turbidity decreased with the increase in the settling time. This is in sharp contrast to the Fe(II) experiments where there was generally an increase in turbidity after 15 min. Second, in general the higher the Al(III) and Fe(III) dosages the lower was the settled solution turbidity. This is also in contrast to the Fe(II) case where the higher the Fe(II) dosage, the greater was the turbidity of the settled solution. Third, at all ratios of Al(III)- and Fe(III)-to-orthophosphate equivalence ratios tested the settling was nearly complete after 30 min. With Fe(II), on the other hand, all samples contained substantial amounts of turbidity even after standing overnight. The orthophosphate removal data for Al(III) and Fe(III) indicate that although the removal by settling was higher for samples with lower residual turbidity, the phosphate concentration in an aliquot of settled sample was not directly

TABLE 16

SETTLING CHARACTERISTICS OF THE PRECIPITATES IN ORTHOPHOSPHATE PRECIPITATION FROM SECONDARY EFFLUENT WITH Al(III)[a]

Exp. No.	Al(III)/PO_4^{-3} Equivalence Ratio	pH[b]	Turbidity of Samples After Indicated Periods of Settling[c] (JTU)					Orthophosphate Removal After 2 hr of Settling (%)	
			5 min	15 min	30 min	1 hr	2 hr	Unfiltered	Filtered
27	0.4	7.48	9.0	6.9	5.4	5.1	5.0	23	32
28	0.8	7.28	5.4	4.7	3.7	3.6	3.4	47	50
29	1.0	7.18	7.3	4.7	4.2	3.9	3.6	59	63
30	1.2	7.09	8.2	4.7	4.0	3.7	3.7	64	69
31	1.5	7.09	6.8	3.2	2.7	2.6	2.3	81	85
32	2.0	6.90	6.5	3.8	2.7	2.3	2.1	91	95

[a] Wastewater #4, Table 1

[b] pH measured after 2 hr of settling

[c] Turbidity analysis made on sample aliquots removed from about 2.5 in. below the water surface

TABLE 17

SETTLING CHARACTERISTICS OF THE PRECIPITATES IN ORTHOPHOSPHATE PRECIPITATION FROM SECONDARY EFFLUENT WITH Fe(III)[a]

Exp. No.	$Fe(III)/PO_4^{-3}$ Equivalence Ratio	pH[b]	Turbidity of Samples After Indicated Periods of Settling[c] (JTU)					Orthophosphate Removal After 2 hr of Settling (%)	
			5 min	15 min	30 min	1 hr	2 hr	Unfiltered	Filtered
33	0.4	7.59	13	7.8	7.6	7.4	7.1	16	28
34	0.8	7.31	13	7.4	6.4	6.0	5.9	39	45
35	1.0	7.19	13	8.2	6.9	6.6	6.4	48	55
36	1.2	7.15	13	7.2	6.5	6.2	6.8	57	63
37	1.5	7.01	14	7.4	5.7	5.2	5.0	72	77
38	2.0	6.80	8.5	6.4	4.8	3.9	3.7	90	93

[a] Wastewater #5, Table 1

[b] pH measured after 2 hr of settling

[c] Turbidity analysis made on sample aliquots removed from about 2.5 in. below the water surface

proportional to its turbidity content. In all cases the degree of phosphate removal achieved by plain sedimentation and by filtration increased with the Al(III) and Fe(III) dosages used. For the lowest and highest Al(III) doses, phosphate removals were 32 and 95% for the filtrates and 23 and 91% for the unfiltered samples. The corresponding phosphate removal values for Fe(III) were 28 and 93% for the filtrates and 16 and 90% for unfiltered samples, respectively.

In summary, in the precipitation of phosphates from secondary effluent, the settling properties of the precipitates formed with Al(III) and Fe(III) are superior to those formed with Fe(II). Thus, while plain sedimentation is generally adequate for the removal of the Fe(III)- and Al(III)-phosphate precipitates, adjustment of pH, addition of polyelectrolyte or process modification would be required for effective removal of the precipitates formed with Fe(II). However, as was discussed before, the poor settling behavior of the precipitates formed with Fe(II) should not be a problem when ferrous iron is added to the wastewater ahead of activated sludge.

Advantages of the Use of Ferrous Iron for Phosphate Precipitation

The use of ferrous iron for phosphate precipitation from wastewater has potentially two major advantages over other precipitation techniques. First, because of the existence of oxidative conditions in conventional biological wastewater treatment, ferrous iron added to the wastewater is oxidized in situ resulting in the homogeneous generation of ferric iron. Homogeneously generated ferric iron is a more efficient phosphate precipitant than ferric iron added from an external source. Second, in some metropolitan areas (e.g., those in the Great Lakes region) waste pickle liquor from local steel industries may provide an inexpensive source of ferrous iron. The cost of acid pickle liquor is generally determined by the transportation cost which is in turn dependent on the hauling distance. The chemical costs of wastewater treatment with pickle liquor at Texas City, Texas, and at Mentor, Ohio, have been estimated at 1.5 and 2¢/lb of iron (0.18¢ and 0.25¢/gm-mole of Fe), respectively.[2] In comparison, the cost of alum is about 24¢/lb of Al or 1.43¢/gm-mole of Al.[2] Although in recent years a number of large-scale experiments have been conducted to assess the effectiveness of Fe(II) for phosphate precipitation, because of the lack of a basic understanding of the chemistry involved, a trial-and-error approach has been used in these evaluation tests. Accordingly, the results of these experiments are not believed to represent the optimum utilization of ferrous iron, although they nevertheless point out the economic attractiveness of wastewater treatment with

Fe(II). For example, at Grayling and Lake Odessa, Michigan, treatment plants where phosphate was precipitated by chemical addition in the primary (34 to 57 mg/ℓ $FeCl_2$, 12 to 14 mg/ℓ NaOH, 0.3 to 0.5 mg/ℓ anionic polymer), total operating costs are estimated to range from a possible low of $0.01/1000 gal. to a high of $0.05/1000 gal.[2] The chemical costs for Mentor, Ohio, utilizing waste pickle liquor, are estimated to be $0.023/1000 gal. with an additional cost of $0.01/1000 gal. for handling the excess sludge produced by chemical precipitation.[2] In comparison, for a wastewater containing 10 mg/ℓ P phosphate, the total costs for 90% phosphate removal by addition of aluminum in the primary stage are estimated at $0.036/1000 gal.[2]

Section II of this report contains recommendations for a study which will seek to define the optimum conditions for effective utilization of ferrous iron in wastewater treatment. Unless such a study is undertaken, the economics of the phosphate precipitation by addition of ferrous iron cannot be accurately defined.

SECTION VI

ACKNOWLEDGMENTS

The support of this project by the Water Quality Office, Environmental Protection Agency, is acknowledged with gratitude. Sincere thanks are due to Dr. Sidney A. Hannah, the Project Officer, and Mr. Jesse M. Cohen, Chief, Physical and Chemical Treatment Research, both of the Cincinnati Advanced Waste Treatment Research Laboratory, for the interest, expertise and guidance provided during the course of this investigation.

The help provided by the director and staff of the Las Virgenes Municipal Water District, Calabasas, California, in providing wastewater samples is gratefully acknowledged.

At Atomics International, Drs. Masood Ghassemi and Howard L. Recht were, respectively, the principal investigator and program manager for this project. Most of the laboratory work was performed by Miss Nancy M. Trahey. Special thanks are due to Drs. Donald E. McKenzie, Eugene V. Kleber and Samuel J. Yosim for their critical review of the manuscript and for their numerous helpful suggestions during the course of this work. Finally, special thanks are due to Mrs. Evelyn Cress for typing the final manuscript and for her numerous other secretarial assistance.

Preceding page blank

SECTION VII

REFERENCES

1. Nesbitt, J. B., "Removal of Phosphorus from Municipal Sewage Plant Effluents," Engineering Research Bulletin B-93, Pennsylvania State University, University Park, Pa. (1966).

2. Convery, J. J., "The Use of Physical-Chemical Treatment Techniques for the Removal of Phosphorus from Municipal Wastewaters," Advanced Waste Treatment Seminar, jointly sponsored by California State Water Resources Control Board and Pacific Southwest Regional Office of FWQA, San Francisco, Calif., Oct. 28 and 29, 1970.

3. Stumm, W., Discussion in "Advances in Water Pollution Control Research," Proc. 1st Intl. Conf. Water Poll. Res., Pergamon Press Ltd., London, England, Vol. 2, 216 (1964).

4. Recht, H. L. and Ghassemi, M., "Kinetics and Mechanism of Precipitation and Nature of the Precipitate Obtained in Phosphate Removal from Wastewater Using Aluminum(III) and Iron(III) Salts," Water Pollution Control Research Series 17010EKI 04/70, U. S. Dept. of the Interior, FWQA (1970)

5. Cohen, J. M., "Improved Jar Test Procedure," J. Am. Water Works Assoc., 49, p 1425 (1966).

6. Manual on Industrial Water and Industrial Waste Water, 2nd Ed., ASTM Special Publication No. 148-I (1966).

7. Instruction Manual for Titrator Type TTT11, Radiometer Co., Copenhagen, Denmark.

8. Hush, N. S., "Intervalence-Transfer Absorption. Part 2. Theoretical Considerations and Spectroscopic Data," in Progress in Organic Chemistry, F. A. Cotton, Ed., Vol. 8, Interscience Publishers, New York (1967)

9. Singer, P. C., "Anaerobic Control of Phosphates by Ferrous Iron," Paper presented at the 43rd Annual Conference, Water Pollution Control Federation, Boston, Mass., Oct. 1970.

Preceding page blank

10. Sillen, L. G., and Martell, A. E., "Stability Constants of Metal-Ion Complexes," Spec. Publ. No. 17, The Chemical Society, London, Burlington House (1964)

11. Van Wazer, J. R., "Phosphorus and Its Compounds," Interscience Publishers, New York (1958).

12. Leussing, D. L., and Kolthoff, I. M., "The Solubility Product of Ferrous Hydroxide and Ionization of the Aquo-Ferrous Ion," J. Am. Chem. Soc., 75, p 2376 (1953).

13. Gayer, K. H., and Woentner, L., "The Solubility of Ferrous Hydroxide and Ferric Hydroxide in Acidic and Basic Media at 25°," J. Phys. Chem., 60, p 1569 (1956).

14. Galal-Gorchev, H., and Stumm, W., "The Reaction of Ferric Iron with Orthophosphate," Incrg. Nucl. Chem., 25, p 567 (1963).

15. Stumm, W., and Lee, F., "Oxygenation of Ferrous Iron," Ind. and Eng. Chem., 53, p 143 (1961).

16. Robinson, L. R., "The Effect of Organic Materials on Iron Removal from Ground Water," Water and Sewage Works, 114, p 337 (1967)

17. Singer, P. C., and Stumm, W., "Oxygenation of Ferrous Iron," Water Pollution Control Research Series DAST-28, U. S. Dept. of the Interior, FWQA (1969).

18. Wukasch, R. D., "The Dow Process for Phosphorus Removal," FWQA Phosphorus Removal Symposium, Chicago, Ill., June 1968.

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

1. Report No.
2.
3. Accession No. W

4. Title

PHOSPHATE PRECIPITATION WITH FERROUS IRON

5. Report Date
6.
8. Performing Organization Report No.

7. Author(s)

Ghassemi, M., and Recht, H. L.

9. Organization

Atomics International
A Division of North American Rockwell Corporation
Canoga Park, California

10. Project No.

17010 EKI

11. Contract/Grant No.

12. Sponsoring Organization

13. Type of Report and Period Covered

15. Supplementary Notes

16. Abstract

Phosphate removal by ferrous iron addition was studied in batch precipitation tests conducted on pure solutions of ortho-, pyro- and tripolyphosphate, orthophosphate solutions containing bicarbonate ion, and secondary effluent. The effects of pH and reactant concentration on the efficiency of reactant removal were evaluated.

In the absence of dissolved oxygen and for initial conditions of 12 mg/l P and a reactant equivalence ratio of 1.0, orthophosphate removal was maximum (97%) at a pH of 8.0. The precipitate formed was identified as vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$. At this pH and lower pH levels, Fe(II) removal nearly paralleled that of orthophosphate removal. The time for maximum orthophosphate removal increased with decreasing pH. The reaction speed was independent of Fe(II) concentration but decreased at lower orthophosphate levels. The system behavior was the same in secondary effluent as in pure solutions. Pyro- and tripolyphosphates were less efficiently precipitated than orthophosphate. Dissolved oxygen increased orthophosphate removal efficiency. However, the precipitates obtained in the treatment of oxygen-containing secondary effluent were usually very fine and did not settle well. The data on Fe(II)-phosphate precipitation are compared with those of Fe(III)- and Al(III)-phosphate systems.

17a. Descriptors

*Phosphates, *Chemical precipitation, *Waste water treatment, Eutrophication, Water pollution control

17b. Identifiers

*Ferrous phosphate, *Phosphate precipitation, Ferrous salts, Reaction rate

17c. COWRR Field & Group

18. Availability

19. Security Class. (Report)

20. Security Class. (Page)

21. No. of Pages

22. Price

Send To:

WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

Abstractor

Institution